Technical and economic aspects of furfural and ethanol coproduction from sugarcane bagasse and harvest residues, annexed to a sugar mill

by

# Rhulani Nicolas Ntimbani

Dissertation presented for the Degree

of

# Doctor of Philosophy (Chemical Engineering)

in the Faculty of Engineering at Stellenbosch University

The financial assistance of the National Research Foundation (NRF) towards this research is hereby acknowledged. Opinions expressed and conclusions arrived at, are those of the author and are not necessarily to be attributed to the NRF

Supervisor Prof. Johann F. Görgens

*Co-Supervisor* Dr. Somayeh Farzad

March 2021

## DECLARATION

By submitting this thesis electronically, I declare that the entirety of the work contained therein is my own, original work, that I am the sole author thereof (save to the extent explicitly otherwise stated), that reproduction and publication thereof by Stellenbosch University will not infringe any third party rights and that I have not previously in its entirety or in part submitted it for obtaining any qualification.

Date: .....

This dissertation includes two original papers published in peer-reviewed journals and one unpublished manuscript which will be submitted to peer reviewed international journal for publication. The development and writing of the papers (published and unpublished) were the principal responsibility of myself and, for each of the cases where this is not the case, a declaration is included in the dissertation indicating the nature and extent of the contributions of co-authors.

> Copyright © 2021 Stellenbosch University All rights reserved

### PLAGIARISM DECLARATION

- 1. Plagiarism is the use of ideas, material and other intellectual property of another's work and to present it as my own.
- 2. I agree that plagiarism is a punishable offence because it constitutes theft.
- 3. I also understand that direct translations are plagiarism.
- 4. Accordingly all quotations and contributions from any source whatsoever (including the internet) have been cited fully. I understand that the reproduction of text without quotation marks (even when the source is cited) is plagiarism.
- 5. I declare that the work contained in this assignment, except where otherwise stated, is my original work and that I have not previously (in its entirety or in part) submitted it for grading in this module/assignment or another module/assignment.

Student number: 19590059

Initials and surname: RN Ntimbani

Signature: .....

Date: .....

#### Abstract

Lignocellulose biomass has potential to reduce the consumption of fossil resources. Furfural and ethanol are some of the most promising bioproducts that can be produced from lignocellulose biomass, with the potential to replace fossil-based products. Commercial furfural production is performed in a one-stage process, where furfural is recovered in the vapour phase leaving the reactor. Furfural may also be produced using a two-stage process, whereby lignocelluloses are fractionated into hemicellulose-rich hydrolysate and cellu-lignin solid residues, followed by conversion of the solubilised hemicelluloses into furfural in a subsequent process unit. Conditions of the one-stage furfural process reduce biomass recalcitrance but tend to degrade cellulose components and produce yeast inhibitors. In contrast, conditions in the two-stage furfural process minimise cellulose degradation, while increasing enzymatic susceptibility of residual biomass.

Most studies that consider ethanol production from the cellu-lignin residues from the one-stage furfural process include washing and/or chemical pretreatments prior to fermentation, which increases processing costs. Conversely, residual solids from steam explosion applied in the first stage of the two-stage process, do not require further pretreatment prior to fermentation, in cases where inhibitor resistant yeast strains are used. However, furfural produced from the hemicellulose hydrolysate in the second stage of this process is often recovered and purified using organic solvents that will negatively affect the environment.

Therefore, this study compared the technical and economic differences between the one-stage and two-stage methods of co-producing furfural and ethanol from sugarcane lignocelluloses. One-stage furfural production was achieved in the temperature range of 170-200°C and acid doses of 0-2 wt.% H<sub>2</sub>SO<sub>4</sub> using sugarcane bagasse, with unwashed solid

iii

residues used for ethanol production. Pretreated lignocelluloses from the two-stage furfural production process were similarly assessed for ethanol production. Mass and energy balances for alternative biorefinery scenarios co-producing furfural and ethanol in the one-stage or two-stage configurations, were obtained with Aspen Plus® V8.8 process simulations, using experimental data either collected in this study or published. The internal rate of return (IRR) of the most promising one-stage furfural and ethanol co-production biorefinery was 12.78%, while the equivalent two-stage biorefinery obtained an IRR of 13.59%. The lowest minimum ethanol selling prices (MESPs) achieved by the one-stage furfural and ethanol co-production biorefineries were 1.14 US\$/L and 2.54 US\$/L at a desired IRR of 15 and 20%, respectively. The two-stage furfural and ethanol co-production biorefinery achieved economic indicators that were improved by 36-51%, as demonstrated by the lowest MESPs 0.73 US\$/L and 1.25 US\$/L (at IRRs of 15 and 20%, respectively), in comparison to the one-stage furfural and ethanol co-production biorefinery. One-stage furfural production resulted in significant degradation of cellu-lignin residues, which negatively affected ethanol yield, and the profitability. Improvements in ethanol production due to preservation of cellu-lignin residues in the two-stage furfural production process provided economic benefits. However, the economic potential of furfural and ethanol co-production remained significantly hindered by process energy demands, in the context of energy self-sufficient biorefinery reliant on available feedstock for energy supply. These energy demands decrease the financial viability of furfural production compared to alternative potential co-products.

#### Opsomming

Lignosellulose biomassa het potensiaal om die verbruik van fossielhulpbronne te verminder. Furfuraal en etanol is van die mees belowende bioprodukte wat geproduseer kan word uit lignosellulose biomassa, met die potensiaal om fossielgebaseerde produkte te verplaas. Kommersiële furfuraalproduksie word uitgevoer in 'n een-stap proses, waar furfuraal herwin word uit die dampfase wat die reaktor verlaat. Furfuraal kan ook geproduseer word deur 'n twee-stap proses te gebruik, waar lignosellulose gefraksioneer word in hemisellulose-ryke hidrolisaat en sellulignienvastestofresidu's, gevolg deur omsetting van die oplosbaargemaakte hemisellulose na furfuraal in 'n opvolgende proseseenheid. Kondisies van die eenfase furfuraalproses verminder biomassa weerspannigheid maar neig om sellulosekomponente te verminder en gisinhibeerders te produseer. In kontras, kondisies in die twee-fase furfuraalproses minimeer sellulose afbreking, terwyl ensimatiese vatbaarheid van residuele biomassa verhoog word.

Meeste studies wat etanolproduksie vanuit die sellulignienresidu's van die een-stap furfuraalproses oorweeg, sluit wassery en/of chemiese voorbehandeling voor fermentasie in, wat proseskostes verhoog. Omgekeerd, residuele vastestowwe van stoomontploffings toegepas in die eerste stap van die twee-stap proses het nie verdere voorbehandeling nodig voor fermentasie nie, in gevalle waar inhibeerder-bestande gislyne gebruik word. Furfuraal geproduseer uit die hemisellulose hidrolisaat in die tweede stap van hierdie proses, word egter gereeld herwin en gesuiwer deur organiese oplosmiddels te gebruik wat die omgewing negatief beïnvloed.

Daarom het hierdie studie die tegniese en ekonomiese verskille tussen die een-stap en tweestap metodes van ko-produksie van furfuraal en etanol uit suikerriet lignosellulose vergelyk.

v

Een-stap furfuraalproduksie is bereik in die temperatuurbestek van 170 - 200 °C en suurdosisse van 0 – 2 wt.%  $H_2SO_4$  deur suikerrietbagasse te gebruik, met ongewaste vastestofresidu's gebruik vir etanolproduksie. Voorbehandelde lignosellulose uit die tweestap furfuraalproses is ook gebruik vir etanolproduksie. Massa- en energiebalanse vir alternatiewe bioraffinadery scenario's wat furfuraal en etanol in die een-stap en twee-stap konfigurasies ko-produseer, is verkry met Aspen Plus® V.8.8 prosessimulasies deur eksperimentele data te gebruik wat óf in die studie versamel, óf gepubliseer is. Die interne opbrengskoers (IRR) van die mees belowende een-stap furfuraal en etanol ko-produksie bioraffinadery was 12.78%. terwyl die ekwivalente twee-stap bioraffinadery 'n IRR van 13.59% verkry het. Die laagste minimum etanol verkoopspryse (MESPs) bereik deur die eenstap furfuraal en etanol bioraffinaderye was 1.14 US\$/L en 2.54 US\$/L by 'n gewenste IRR van 15 en 20%, onderskeidelik. Die twee-stap furfuraal en etanol ko-produksie bioraffinadery het ekonomiese indikators bereik wat met 36 - 51% verbeter het, soos gedemonstreer deur die laagste MESPs 0.73 US\$/L en 1.25 US\$/L (by IRRs van 15 en 20%, onderskeidelik), in vergelyking met die een-stap furfuraal en etanol ko-produksie bioraffinadery. Een-stap furfuraalproduksie het beduidende afbreking van sellulignienresidu's tot gevolg gehad, wat etanolopbrengs en winsgewendheid negatief beïnvloed het. Verbeteringe in etanolproduksie as gevolg van preservering van sellulignienresidu's in die twee-stap furfuraalproduksieproses het ekonomiese voordele verskaf. Die ekonomiese potensiaal van furfuraal en etanol koproduksie bly egter beduidend verhinder deur prosesenergievereistes, in die konteks van beperkte energieverskaffing in 'n energie self-onderhoudende bioraffinadery. Hierdie energievereistes verminder die finansiële lewensvatbaarheid van furfuraalproduksie in vergelyking met alternatiewe potensiële ko-produkte.

vi

# Dedication

This work is dedicated to my late grandparents (Khazamula and Madzivandlela Ntimbani), parents (Tsakani and Thompson Ntimbani), my wife (Ingrid Nkuna) and siblings (Moxe, Jimmy, Doctor, Dingani, Doreen and Tlangelani)

#### Acknowledgements

I am grateful to my supervisor Prof. Görgens for welcoming me into the Bioresource Engineering research group (Stellenbosch University) and for providing guidance and support throughout the course of this work.

I am also grateful to my co-supervisor Dr Farzad for providing guidance and support in execution of this work. I also extend my gratitude to the contributions of Dr Haigh and Dr Danon who were initially my co-supervisors.

My gratitude is also extended to the entire Bioresource Engineering research group for the interesting technical discussions, assistance and creating a conducive environment for conducting my research (laboratory experiments and office work). I appreciate the input of Dr Mandegari, Dr Petersen, Dr Diedericks and Dr Brandt. I also thank Prof Dorfling for allowing me to use the pressure reactor in the hydrometallurgy lab for my furfural experiments. I also thank Irene and Andrew for sharing their experiences of the furfural reactor and for cooperation as we shared workspace used for furfural experiments. I also extend my gratitude to Levine Simmers for assistance with sample analysis by HPLC and Henry Solomon for assistance with biomass compositional analysis. I also thank the Process Engineering Department workshop staff and all other support staff for their assistance. I am grateful to Martin for sharing his sugarcane bagasse that I used as feedstock for my experiments and Lukas for training on operation of sand bath equipment. I am also grateful to Pfariso Maumela for showing me how to prepare HPLC samples and operating other equipment/machinery used to complete this work.

I am thankful to funding of this work from National Research Foundation (NFR), Centre of Renewable and Sustainable Energy Studies (CRSES) and Sugar Milling Research Institute

viii

(SMRI). I am also Thankful to Illovo for hosting me at their Sezela furfural plant where I conducted furfural work using their pilot reactor. I am also grateful to RCL for allowing me to ferment some of their samples.

I also acknowledge the love, support and motivation from my family, friends and former teachers. I appreciate the inspiring words and all sorts of support from Jimmy. I also thank my wife for her support, patience and encouragement.

I thank God for the strength and guidance throughout the course of this research work.

# Contents

DECLARATIONi				
PLAGIARISM DECLARATIONii				
Abstractiii				
Opsommingv				
Acknowledgements viii				
Chapter 1: Introduction1				
1.1	Bacl	ckground and motivation1		
1.2	Nov	elty of the study5		
1.3	Diss	sertation layout6		
Chapter 2: Literature review23				
2.1	Intro	oduction23		
2.2	Furf	ural production25		
2.3	Furf	ural production methods28		
2.3	.1	One-stage furfural production (Direct furfural method)28		
2.3	.2	Two-stage furfural production (Indirect furfural method)33		
2.4 Ethanol production from lignocellulosic biomass				
2.5	Sole	production of ethanol, or its co-production with furfural		
2.6	Inte	gration of furfural and ethanol production42		
2.7 Conclusions				
2.7.1		Furfural production and corresponding ethanol yield from residual biomass .50		
2.7.2		Economics of the one-stage furfural process and ethanol co-production by SSF 51		
2.7.3 versus tv		Techno-economic aspects of one-stage furfural and ethanol co-production wo-stage furfural and ethanol co-production51		
Chapter 3: Research aim and objectives69				
3.1 Contribution 1: Experimental investigation into one-stage furfural production followed by ethanol production from furfural solid residues				
3.1.1		Statement of Novelty69		
3.1.2		Research objectives70		
3.2 Contribution 2: Process simulations and techno-economics of one-stage furfural production followed by ethanol production from furfural solid residues7				
3.2.1		Statement of Novelty71		
3.2.2		Research objectives71		

3.3 Contribution 3: Techno-economic aspects of one-stage furfural and ethanol co-			
production versus two-stage furfural and ethanol co-production			
3.3.1 Statement of Novelty72			
3.3.2 Research objectives73			
Chapter 4: One-stage furfural and ethanol co-production74			
Chapter 5: Techno-economics of one-stage furfural and ethanol co-production			
Chapter 6: Techno-economics of one-stage and two-stage furfural production from sugarcane lignocelluloses, with ethanol co-production			
Chapter 7: Conclusions and Recommendations179			
7.1 Summary of main findings from contributions of research179			
7.1.1 Contribution 1: One-stage furfural production followed by ethanol production from furfural solid residues			
7.1.2 Contribution 2: One-stage furfural production followed by ethanol production from furfural solid residues			
7.1.3 Contribution 3: Techno-economic aspects of one-stage furfural and ethanol co- production versus two-stage furfural and ethanol co-production			
7.2 Overall Conclusions			
7.3 Recommendations			
7.3.1 Optimisation of furfural residues fermentation and scale-up studies			
7.3.2 Development of one-stage furfural reactor and furfural distillation optimisation			
7.3.3 Life cycle assessment and process flowsheet develop of the two-stage furfural process using reactive distillation as furfural reactor			
Supplementary data for Chapter 4187			
Supplementary data for Chapter 6191			

#### **Chapter 1: Introduction**

#### 1.1 Background and motivation

Most fuels and chemicals consumed worldwide are derived from fossil resources and considering environmental and political concerns and increased consumption in developing countries, alternative sustainable resources are needed (Jin et al., 2019; Kazi et al., 2011). Sugarcane bagasse and harvest residues are lignocellulosic materials that offer alternative resources and are renewable resources (Mohlala et al., 2016; Smithers, 2014). In South Africa, sugarcane bagasse is annually produced at approximately seven million tons (Mohlala et al., 2016; Smithers, 2014). Sugarcane bagasse is generally used as fuel to meet sugar mill energy requirements through combustion in energy plants that operate inefficiently (Clauser et al., 2016). Effective steam utilization by the sugar mills coupled with upgrades in boilers will decrease bagasse consumption by energy plants by about 50% (Clauser et al., 2016; Rocha et al., 2012). Therefore, improvements in sugar mill energy plants and harvesting methods will result in excess sugarcane bagasse and harvest residues available for valorisation as an alternative to fossil resources (Qing et al., 2017; Schmidt et al., 2017; Smithers, 2014).

Furfural and bioethanol are some of the promising biochemical products that can be co-produced from the hemicellulose and cellulose components of lignocellulosic biomass, respectively. Generally, the pretreatment step employed to reduce biomass recalcitrance and make it amenable to hydrolysis-fermentation to ethanol, is the most capital and energy intensive step in this process (Cardona et al., 2010; Zabed et al., 2017). Since furfural is only produced from hemicellulose, the one-stage furfural process offers the advantage of performing two functions simultaneous in one reactor, that is furfural production and ethanol

pretreatment, while providing cellu-lignin residues for ethanol production, which may improve the overall ethanol process economics (Avci et al., 2013; Mesa et al., 2014).

Although furfural and ethanol are produced from different components of the lignocellulosic biomass, ethanol production from cellu-lignin residues produced after the onestage furfural method, may be negatively affected by highly severe furfural production conditions, affecting the suitability of these as raw materials for cellulosic ethanol production (Cardona et al., 2010; Watanabe et al., 2019). The negative effects include cellulose degradation and yeast inhibition caused by the formation of acetic acid, formic acid, phenols, 5-hydroxymethylfurfural (5-HMF) and furfural under harsh conditions of the one-stage furfural process (Watanabe et al., 2019; Xu et al., 2019). Moreover, pseudo-lignin formation is more prevalent under such severe conditions and it causes a decrease in ethanol yield as it inhibits yeast and reduce cellulose accessibility by enzymes (Hu et al., 2012). Reducing the furfural process severity can prevent cellulose degradation and may increase in ethanol production provided the residual solids are enzymatically digestible, however, furfural yield will be decreased due to reduced extent of xylose conversion to furfural at low severities (Avci et al., 2013; Mesa et al., 2014).

An alternative to the one-stage furfural process is the two-stage furfural process, which uses steam explosion pretreatment to selectively remove hemicelluloses from lignocelluloses, while preserving cellulose in the solid residues and increasing its suitability for enzymatic hydrolysis (Mokomele et al., 2018; Neves et al., 2016). In the two-stage furfural process, the xylose rich hydrolysate is used as furfural feedstock and is obtained from liquid separated from steam explosion pretreated residual solid (Chen et al., 2015), while the solid residues are applied for ethanol production. The two-stage furfural method permits the use

of optimal conditions for furfural formation, whereas the use of furfural optimal conditions in the one-stage furfural method reduces the yield of ethanol because of formation of inhibitors and cellulose degradation (Avci et al., 2013; Raman and Gnansounou, 2015). The main disadvantage of the two-stage furfural process is the use of organic solvents to purify and recover furfural product (Farzad et al., 2017). Previous studies have shown that the use of organic solvents causes environmental problems and increases energy demands as they need to be recovered to minimise operational costs (Farzad et al., 2017; Zhao and Liu, 2019)

The effects of the one-stage furfural production conditions on ethanol production are not clearly outlined in literature, especially for the South African sugarcane bagasse. As such, there is insufficient data that can be used to develop process flowsheet for an integrated onestage furfural and ethanol biorefinery, which can be subsequently used to assess technoeconomic aspects of such a biorefinery configuration. Although there are several studies that consider techno-economic aspects of two-stage furfural and ethanol co-production (Farzad et al., 2017; Xing et al., 2011; Zang et al., 2020; Zhao and Liu, 2019), most of these studies suggest the use of organic solvents for furfural purification and recovery.

Therefore, the aim of this study was to evaluate the effects of the one-stage furfural production conditions on ethanol production from unwashed residual biomass thereby generating furfural and ethanol yield data at various operating conditions. The study also included investigation of technical and economic aspects of the one-stage furfural and ethanol integrated biorefinery configuration. Technical and economic aspects of the twostage furfural process integrated with ethanol without the use of organic solvents for furfural separation were also studied and compared to the one-stage furfural and ethanol integrated biorefinery configuration. Conventional distillation configuration used for separation and

recovery of furfural from one-stage furfural production was applied in the two-stage furfural and ethanol biorefinery to avoid negative environmental effects posed by the use of organic solvents. In essence, the study will determine whether the two-stage furfural process results in improved furfural and ethanol yields than the one-stage, despite the technical compromise between furfural and ethanol yields in either processes. The study also determines whether the expected increase in yields from the two-stage process will result in better economic outcome than the one-stage process, despite larger processing costs of the former.

To achieve the aims and objectives of the study, one-stage furfural experimental work in the temperature range 170-200°C and acid doses of 0-2 wt.% sulphuric acid was conducted using sugarcane bagasse. Subsequently, ethanol experiments were carried out using furfural residues as feedstock where Ethanol Red<sup>®</sup> and CelluX<sup>™</sup>4 were employed as fermentation yeast strains. Furfural and ethanol yield data obtained from one-stage furfural experiments were used to generate mass and energy balances for one-stage furfural and ethanol coproduction biorefinery in Aspen Plus® V8.8 to estimate capital and operating costs. Steam explosion was used for the two-stage furfural process where xylose rich hydrolysate is produced and used as furfural feed. Likewise, mass and energy balances for two-stage furfural and ethanol co-production biorefinery were also generated in Aspen Plus® V8.8 utilising data from previous research and own furfural yield data from steam explosion hydrolysate. The study also included techno-economics of biorefineries focussed on sole production of ethanol and furfural developed using literature data. Internal rate of return (IRR) and minimum ethanol selling price (MESP) were computed to indicate profitability of all the developed biorefineries and to determine improvement in ethanol economics.

#### **1.2 Novelty of the study**

Studies utilising lignocellulose as feedstock for co-production of ethanol from nondetoxified furfural residues produced using the one-stage furfural production method at various process conditions are scarce. This study evaluated the effects of the one-stage furfural production conditions on the yields of both furfural and ethanol production when using the simultaneous saccharification and fermentation (SSF) technique without washing (detoxification) and delignification of residual biomass before fermentation. This study showed the relationship between furfural and ethanol yields and at the same time generated furfural and ethanol yield data from lignocellulose that is needed for development of biorefinery process flowsheet.

Techno-economic assessment of integrated one-stage furfural and ethanol coproduction biorefinery developed using actual experimental data from furfural and ethanol experimental work using sugarcane bagasse as feedstock was conducted. Although the data used to generate mass and energy balance was obtained from experiments utilising sugarcane bagasse as feedstock, the study gave an indication of expected technical and economic aspects associated with the one-stage furfural and ethanol co-production from lignocellulosic feedstock. The technical aspects included effects of energy demands on overall productivity since energy self-sufficient biorefinery concept was applied in process flowsheet development, required energy demands (steam and electricity) as well as expected productivity.

Techno-economic assessment of integrated two-stage furfural and ethanol coproduction biorefinery was also carried out and the biorefinery flowsheet were developed

using literature data and own furfural experimental work from steam explosion hydrolysate sugarcane bagasse as feedstock. Studies in which techno-economics of the one-stage furfuralethanol co-production and the two-stage furfural-ethanol biorefinery configurations are compared are scarce in literature. Moreover, techno-economic studies in literature employ different economic parameters and costing methods that make it difficult to compare economic viability of processes evaluated in different studies. Thus, this study provided a techno-economic analysis of both one-stage and two-stage furfural production method where ethanol is produced alongside in an energy self-sufficient biorefinery. The results from this study can assist in selecting process configuration for co-production of ethanol and furfural. Additionally, this study can influence financial decisions about lignocellulosic ethanol and furfural co-production and contribute towards development of the bioeconomy.

#### **1.3 Dissertation layout**

The layout of this study entails seven chapters including the introduction, which is Chapter 1. The introduction chapter is followed by literature review of relevant concepts outlined in Chapter 2. Research aims and objectives are outlined in Chapter 3 followed by Chapters 4-6 focussed on research contributions and specific research methods employed. Chapter 4 focussed one stage furfural and ethanol co-production experimental work from sugarcane bagasse and the techno-economic aspects of integrated one-stage furfural and ethanol coproduction are reported in Chapter 5. A comparison of technical and economic aspects of the one-stage furfural-ethanol co-production and the two-stage furfural-ethanol biorefinery configurations are reported in Chapter 6. Finally, conclusions and recommendations from the study are detailed in Chapter 7. Schematic representation of the dissertation layout is provided in Figure 1.1.



# Figure 1. 1: Dissertation layout. SE stands for steam explosion and SSF stands for simultaneous saccharification and fermentation.

#### References

Aguilar, R., Ramírez, J.A., Garrote, G., Vázquez, M., 2002. Kinetic study of the acid hydrolysis

of sugar cane bagasse. J. Food Eng. 55, 309-318. https://doi.org/10.1016/S0260-

8774(02)00106-1

- Albers, E., Larsson, C., Liden, G., Niklasson, C., Gustafsson, L., 1996. Influence of the Nitrogen Source on Saccharomyces cerevisiae Anaerobic Growth and Product Formation. Appl. Environ. Microbiol. 62, 3187–3195. doi:10.1128/AEM.62.9.3187-3195.1996
- Avci, A., Saha, B.C., Kennedy, G.J., Cotta, M.A., 2013. High temperature dilute phosphoric acid pretreatment of corn stover for furfural and ethanol production. Ind. Crops Prod. 50, 478–484. https://doi.org/10.1016/j.indcrop.2013.07.055

Bamufleh, H.S., Alhamed, Y.A., Daous, M.A., 2013. Furfural from midribs of date-palm trees by sulfuric acid hydrolysis. Ind. Crop. Prod. 42, 421–428. https://doi.org/10.1016/j.indcrop.2012.06.008

- Biddy, M.J., Scarlata, C., Christopher, K., 2016. Chemicals from Biomass: A Market Assessment of Bioproducts with Near-Term Potential, National Renewable Energy Laboratory.
- Bohre, A., Dutta, S., Saha, B., Abu-omar, M.M., 2015. Upgrading Furfurals to Drop-in
  Biofuels: An Overview. ACS Sustain. Chem. Eng. 3, 1263–1277.
  https://doi.org/10.1021/acssuschemeng.5b00271
- Boshoff, S., Gottumukkala, L.D., Rensburg, E. Van, Görgens, J., 2016. Paper sludge (PS) to bioethanol: Evaluation of virgin and recycle mill sludge for low enzyme , high-solids fermentation. Bioresour. Technol. 203, 103–111. https://doi.org/10.1016/j.biortech.2015.12.028
- Brienzo, M., Fikizolo, S., Benjamin, Y., Tyhoda, L., 2017. Influence of pretreatment severity on structural changes, lignin content and enzymatic hydrolysis of sugarcane bagasse samples. Renew. Energy 104, 271–280. https://doi.org/10.1016/j.renene.2016.12.037
- Bruce, S.M., Zong, Z., Chatzidimitriou, A., Avci, L.E., Bond, J.Q., Carreon, M.A., Wettstein,
  S.G., 2016. Small pore zeolite catalysts for furfural synthesis from xylose and
  switchgrass in a Y-valerolactone/water solvent. J. Mol. Catal. A Chem. 422, 18–22.
  https://doi.org/10.1016/j.molcata.2016.02.025
- Bu, L., Tang, Y., Xing, Y., Zhang, W., Shang, X., Jiang, J., 2014. Comparison of hydrophilic variation and bioethanol production of furfural residues after delignification pretreatment. Biosci. Biotechnol. Biochem. 78, 1435–1443.
   https://doi.org/10.1080/09168451.2014.921556

- Cai, C.M., Zhang, T., Kumar, R., Wyman, C.E., 2014. Integrated furfural production as a renewable fuel and chemical platform from lignocellulosic biomass. J. Chem. Technol. Biotechnol. 89, 2–10. https://doi.org/10.1002/jctb.4168
- Cardona, C.A., Quintero, J.A., Paz, I.C., 2010. Production of bioethanol from sugarcane bagasse: Status and perspectives. Bioresour. Technol. 101, 4754–4766. https://doi.org/10.1016/j.biortech.2009.10.097
- Chen, H., Qin, L., Yu, B., 2015. Furfural production from steam explosion liquor of rice straw by solid acid catalysts (HZSM-5). Biomass and Bioenergy 73, 77–83. https://doi.org/10.1016/j.biombioe.2014.12.013
- Clauser, N.M., Gutiérrez, S., Area, M.C., Felissia, F.E., Vallejos, M.E., 2016. Small-sized biorefineries as strategy to add value to sugarcane bagasse. Chem. Eng. Res. Des. 107, 137–146. https://doi.org/10.1016/j.cherd.2015.10.050
- Dalvand, K., Rubin, J., Gunukula, S., Wheeler, M.C., Hunt, G., 2018. Economics of biofuels : Market potential of furfural and its derivatives. Biomass and Bioenergy 115, 56–63. https://doi.org/10.1016/j.biombioe.2018.04.005
- Danon, B., Marcotullio, G., De Jong, W., 2013. Mechanistic and kinetic aspects of pentose dehydration towards furfural in aqueous media employing homogeneous catalysis. Green Chem. 1–16. https://doi.org/10.1039/b000000x
- Dashtban, M., Technologies, A., Dashtban, M., 2012. PRODUCTION OF FURFURAL: OVERVIEW AND CHALLENGES. J. Sci. Technol. For. Prod. Process. 2, 44–53.
- de Jong, W., Marcotullio, G., 2010. Overview of Biorefineries based on Co-Production of Furfural, Existing Concepts and Novel Developments. Int. J. Chem. React. Eng. 8, 1–24. https://doi.org/10.2202/1542-6580.2174

Deng, A., Lin, Q., Yan, Y., Li, H., Ren, J., Liu, C., Sun, R., 2016. A feasible process for furfural

production from the pre-hydrolysis liquor of corncob via biochar catalysts in a new biphasic system. Bioresour. Technol. 216, 754–760.

https://doi.org/10.1016/j.biortech.2016.06.002

- Dussan, K., Girisuta, B., Haverty, D., Leahy, J.J., Hayes, M.H.B., 2013. Kinetics of levulinic acid and furfural production from Miscanthus×giganteus. Bioresour. Technol. 149, 216–224. https://doi.org/10.1016/j.biortech.2013.09.006
- Farzad, S., Mandegari, M.A., Guo, M., Haigh, K., Shah, N., Görgens, J.F., 2017. Multi-product biorefineries from lignocelluloses: A pathway to revitalisation of the Sugar Industry?
  Biotechnol. Biofuels 10, 1–24. https://doi.org/10.1186/s13068-017-0761-9
- Favaro, L., Viktor, M.J., Rose, S.H., Viljoen-Bloom, M., van Zyl, W.H., Basaglia, M., Cagnin, L.,
   Casella, S., 2015. Consolidated bioprocessing of starchy substrates into ethanol by
   industrial Saccharomyces cerevisiae strains secreting fungal amylases. Biotechnol.
   Bioeng. 112, 1751–1760. https://doi.org/10.1002/bit.25591
- García-Domínguez, M.T., García-Domínguez, J.C., Feria, M.J., Gómez-Lozano, D.M., López, F., Díaz, M.J., 2013. Furfural production from Eucalyptus globulus: Optimizing by using neural fuzzy models. Chem. Eng. J. 221, 185–192.

https://doi.org/10.1016/j.cej.2013.01.099

- Gebreyohannes, S., Neely, B.J., Gasem, K.A.M., 2014. One-parameter modified nonrandom two-liquid (NRTL) activity coefficient model. Fluid Phase Equilib. 379, 196–205. https://doi.org/10.1016/j.fluid.2014.07.027
- Geddes, C.C., Mullinnix, M.T., Nieves, I.U., Hoffman, R.W., Sagues, W.J., York, S.W., Shanmugam, K.T., Erickson, J.E., Vermerris, W.E., Ingram, L.O., 2013. Seed train development for the fermentation of bagasse from sweet sorghum and sugarcane using a simplified fermentation process. Bioresour. Technol. 128, 716–724.

https://doi.org/10.1016/j.biortech.2012.09.121

- Ghosh, D., Dasgupta, D., Agrawal, D., Kaul, S., Adhikari, D.K., Kurmi, A.K., Arya, P.K., Bangwal,
  D., Negi, M.S., 2015. Fuels and chemicals from lignocellulosic biomass: An integrated
  biorefinery approach. Energy and Fuels 29, 3149–3157.
  https://doi.org/10.1021/acs.energyfuels.5b00144
- Giuliano, A., Barletta, D., Poletto, M., 2018. Techno-economic assessment of a lignocellulosic biorefinery co-producing ethanol and xylitol or furfural. https://doi.org/10.1016/B978-0-444-64235-6.50105-4
- Gubicza, K., Nieves, I.U., Sagues, W.J., Barta, Z., Shanmugam, K.T., Ingram, L.O., 2016. Techno-economic analysis of ethanol production from sugarcane bagasse using a Liquefaction plus Simultaneous Saccharification and co-Fermentation process. Bioresour. Technol. 208, 42–48. https://doi.org/10.1016/j.biortech.2016.01.093
- Guo, Z., Olsson, L., 2016. Physiological responses to acid stress by Saccharomyces cerevisiae when applying high initial cell density. 2 FEMS Yeast Res. 16, 1–11. https://doi.org/10.1093/femsyr/fow072
- Hanly, T.J., Henson, M.A., 2014. Dynamic Model-Based Analysis of Furfural and HMF
  Detoxification by Pure and Mixed Batch Cultures of S . cerevisiae and S . stipitis.
  Biotechnol. Bioeng. 111, 272–284. https://doi.org/10.1002/bit.25101
- He, J., Zhang, W., Liu, X., Xu, N., Xiong, P., 2016. Optimization of prehydrolysis time and substrate feeding to improve ethanol production by simultaneous saccharification and fermentation of furfural process residue. J. Biosci. Bioeng. 122, 563–569. https://doi.org/10.1016/j.jbiosc.2016.04.012
- Hernández, V., Romero-garcía, J.M., Dávila, J.A., Castro, E., Cardona, C.A., 2014. Technoeconomic and environmental assessment of an olive stone based biorefinery. Resour.

Conserv. Recycl. 92, 145–150. https://doi.org/10.1016/j.resconrec.2014.09.008

- Himmel, M.E., Ruth, M.F., Wyman, C.E., 1999. Cellulase for commodity products from cellulosic biomass. Curr. Opin. Biotechnol. 10, 358–364. https://doi.org/10.1016/S0958-1669(99)80065-2
- Hossain, S., Theodoropoulos, C., Yousuf, A., 2019. Techno-economic evaluation of heat integrated second generation bioethanol and furfural coproduction. Biochem. Eng. J. 144, 89–103. https://doi.org/10.1016/j.bej.2019.01.017
- Hu, F., Jung, S., Ragauskas, A., 2012. Pseudo-lignin formation and its impact on enzymatic hydrolysis. Bioresour. Technol. 117, 7–12.

https://doi.org/10.1016/j.biortech.2012.04.037

- Humbird, D., Davis, R., Tao, L., Kinchin, C., Hsu, D., Aden, A., 2011. Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol: Dilute-Acid Pretreatment and Enzymatic Hydrolysis of Corn Stover, National Renewable Energy Laboratory.
- Jeon, Y.J., Xun, Z., Rogers, P.L., 2010. Comparative evaluations of cellulosic raw materials for second generation bioethanol production 518–524. https://doi.org/10.1111/j.1472-765X.2010.02923.x
- Ji, H., Chen, L., Zhu, J.Y., Gleisner, R., Zhang, X., 2016. Reaction Kinetics Based Optimization of Furfural Production from Corncob Using a Fully Recyclable Solid Acid. Ind. Eng. Chem. Res. 55, 11253–11259. https://doi.org/10.1021/acs.iecr.6b03243
- Ji, L., Zheng, T., Zhao, P., Zhang, W., Jiang, J., 2016. Ethanol production from a biomass mixture of furfural residues with green liquor-peroxide saccarified cassava liquid. BMC Biotechnol. 16, 1–11. https://doi.org/10.1186/s12896-016-0278-5

Jin, E., Mendis, G.P., Sutherland, J.W., 2019. Integrated sustainability assessment for a

bioenergy system: A system dynamics model of switchgrass for cellulosic ethanol production in the U. S. midwest. J. Clean. Prod. 234, 503–520.

https://doi.org/10.1016/j.jclepro.2019.06.205

Kapanji, K.K., Haigh, K.F., Görgens, J.F., 2019. Techno-economic analysis of chemically catalysed lignocellulose biorefineries at a typical sugar mill : Sorbitol or glucaric acid and electricity. Bioresour. Technol. 289, 121635.

https://doi.org/10.1016/j.biortech.2019.121635

- Katsimpouras, C., Kalogiannis, K.G., Kalogianni, A., Lappas, A.A., 2017. Production of high concentrated cellulosic ethanol by acetone / water oxidized pretreated beech wood. Biotechnol. Biofuels 10, 1–16. https://doi.org/10.1186/s13068-017-0737-9
- Kazi, F.K., Patel, A.D., Serrano-ruiz, J.C., Dumesic, J.A., Anex, R.P., 2011. Techno-economic analysis of dimethylfuran (DMF) and hydroxymethylfurfural (HMF) production from pure fructose in catalytic processes. Chem. Eng. J. 169, 329–338. https://doi.org/10.1016/j.cej.2011.03.018
- Lavarack, B.P., Griffin, G.J., Rodman, D., 2002. The acid hydrolysis of sugarcane bagasse hemicellulose to produce xylose,arabinose,glucose and other products. Biomass and Bioenergy 23, 367–380. https://doi.org/10.1016/S0961-9534(02)00066-1
- Li, H., Wang, X., Liu, C., Ren, J., Zhao, X., Sun, R., Wu, A., 2016. An efficient pretreatment for the selectively hydrothermal conversion of corncob into furfural: The combined mixed ball milling and ultrasonic pretreatments. Ind. Crops Prod. 94, 721–728. https://doi.org/10.1016/j.indcrop.2016.09.052
- Lin, Q., Li, H., Ren, J., Deng, A., Li, W., Liu, C., Sun, R., 2017. Production of xylooligosaccharides by microwave-induced, organic acid-catalyzed hydrolysis of different xylan-type hemicelluloses: Optimization by response surface methodology.

Carbohydr. Polym. 157, 214–225. https://doi.org/10.1016/j.carbpol.2016.09.091

- Liu, L., Chang, H. min, Jameel, H., Park, S., 2018. Furfural production from biomass pretreatment hydrolysate using vapor-releasing reactor system. Bioresour. Technol. 252, 165–171. https://doi.org/10.1016/j.biortech.2018.01.006
- Mandegari, M.A., Farzad, S., Görgens, J.F., 2017a. Economic and environmental assessment of cellulosic ethanol production scenarios annexed to a typical sugar mill. Bioresour. Technol. 224, 314–326. https://doi.org/10.1016/j.biortech.2016.10.074
- Mandegari, M.A., Farzad, S., van Rensburg, E., Görgens, J.F., 2017b. Multi-criteria analysis of a biorefi nery for co-production of lactic acid and ethanol from sugarcane lignocellulose. Biofuels, Bioprod. Biorefining 11, 971–990. https://doi.org/10.1002/bbb
- Mao, L., Zhang, L., Gao, N., Li, A., 2012. FeCl 3 and acetic acid co-catalyzed hydrolysis of corncob for improving furfural production and lignin removal from residue. Bioresour.
   Technol. 123, 324–331. https://doi.org/10.1016/j.biortech.2012.07.058
- Mesa, L., Martínez, Y., Barrio, E., González, E., 2017. Desirability function for optimization of
   Dilute Acid pretreatment of sugarcane straw for ethanol production and preliminary
   economic analysis based in three fermentation configurations. Appl. Energy 198, 299–
   311. https://doi.org/10.1016/j.apenergy.2017.03.018
- Mesa, L., Morales, M., González, E., Cara, C., Romero, I., Castro, E., Mussatto, S.I., 2014.
  Restructuring the processes for furfural and xylose production from sugarcane bagasse
  in a biorefinery concept for ethanol production. Chem. Eng. Process. Process Intensif.
  85, 196–202. https://doi.org/10.1016/j.cep.2014.07.012
- Metkar, P.S., Till, E.J., Corbin, D.R., Pereira, C.J., Hutchenson, K.W., Sengupta, S.K., 2015. furfural using solid acid catalysts †. Green Chem. 17, 1453–1466. https://doi.org/10.1039/c4gc01912a

Mohlala, L.M., Bodunrin, M.O., Awosusi, A.A., Daramola, M.O., Cele, N.P., Olubambi, P.A.,
2016. Beneficiation of corncob and sugarcane bagasse for energy generation and
materials development in Nigeria and South Africa: A short overview. Alexandria Eng. J.
55, 3025–3036. https://doi.org/10.1016/j.aej.2016.05.014

Mokomele, T., Sousa, C., Balan, V., Rensburg, E. Van, Dale, B.E., Görgens, J.F., 2018. Ethanol production potential from AFEX <sup>™</sup> and steam - exploded sugarcane residues for sugarcane biorefineries. Biotechnol. Biofuels 11, 1–21. https://doi.org/10.1186/s13068-018-1130-z

- Moncada, J., Cardona, C.A., Higuita, J.C., Vélez, J.J., López-Suarez, F.E., 2016. Wood residue (Pinus patula bark) as an alternative feedstock for producing ethanol and furfural in Colombia: Experimental, techno-economic and environmental assessments. Chem. Eng. Sci. 140, 309–318. https://doi.org/10.1016/j.ces.2015.10.027
- Neves, P. V, Pitarelo, A.P., Ramos, L.P., 2016. Production of cellulosic ethanol from sugarcane bagasse by steam explosion: Effect of extractives content, acid catalysis and different fermentation technologies. Bioresour. Technol. 208, 184–194. https://doi.org/10.1016/j.biortech.2016.02.085
- Nguyen, T.Y., Cai, C.M., Osman, O., Kumar, R., Wyman, C.E., 2016. CELF pretreatment of corn stover boosts ethanol titers and yields from high solids SSF with low enzyme loadings. Green Chem. 1581–1589. https://doi.org/10.1039/c5gc01977j
- Nhien, L.C., Long, N.V.D., Kim, S., Lee, M., 2016. Design and optimization of intensified biorefinery process for furfural production through a systematic procedure. Biochem.
   Eng. J. 116, 166–175. https://doi.org/10.1016/j.bej.2016.04.002
- Nieder-Heitmann, M., Haigh, K.F., Görgens, J.F., 2018. Process design and economic analysis of a biore fi nery co-producing itaconic acid and electricity from sugarcane bagasse and

trash lignocelluloses. Bioresour. Technol. 262, 159–168.

https://doi.org/10.1016/j.biortech.2018.04.075

- Özüdoğru, H.M.R., Haigh, K.F., Görgens, J.F., 2019. Techno-economic analysis of product biorefineries utilizing sugarcane lignocelluloses : Xylitol , citric acid and glutamic acid scenarios annexed to sugar mills with electricity co-production. Ind. Crop. Prod. 133, 259–268. https://doi.org/10.1016/j.indcrop.2019.03.015
- Pabari, R.M., Ramtoola, Z., 2012. Application of face centred central composite design to optimise compression force and tablet diameter for the formulation of mechanically strong and fast disintegrating orodispersible tablets. Int. J. Pharm. 430, 18–25. https://doi.org/10.1016/j.ijpharm.2012.03.021
- Panahi, H.S.K., Dehhaghi, M., Kinder, J.E., Ezeji, T.C., 2019. A review on green liquid fuels for the transportation sector : a prospect of microbial solutions to climate change. Biofuel Res. J. 23, 995–1024. https://doi.org/10.18331/BRJ2019.6.3.2
- Patel, H., Chapla, D., Shah, A., 2017. Bioconversion of pretreated sugarcane bagasse using enzymatic and acid followed by enzymatic hydrolysis approaches for bioethanol production. Renew. Energy 109, 323–331.

https://doi.org/10.1016/j.renene.2017.03.057

- Petersen, A.M., Haigh, K., Görgens, J.F., 2014. Techno-economics of integrating bioethanol production from spent sulfite liquor for reduction of greenhouse gas emissions from sulfite pulping mills. Biotechnol. Biofuels 7, 1–14. https://doi.org/10.1186/s13068-014-0169-8
- Prajapati, B.P., Jana, U.K., Suryawanshi, R.K., Kango, N., 2020. Sugarcane bagasse sacchari fi cation using Aspergillus tubingensis enzymatic cocktail for 2G bio-ethanol production.
   Renew. Energy 152, 653–663. https://doi.org/10.1016/j.renene.2020.01.063

- Qing, Q., Guo, Q., Zhou, L., Wan, Y., Xu, Y., Ji, H., Gao, X., Zhang, Y., 2017. Catalytic conversion of corncob and corncob pretreatment hydrolysate to furfural in a biphasic system with addition of sodium chloride. Bioresour. Technol. 226, 247–254. https://doi.org/10.1016/j.biortech.2016.11.118
- Raman, J.K., Gnansounou, E., 2015. Furfural production from empty fruit bunch A biorefinery approach. Ind. Crops Prod. 69, 371–377. https://doi.org/10.1016/j.indcrop.2015.02.063
- Rocha, G.J.M., Martin, C., da Silva, V.F.N., Gomez, E.O., Goncalves, A.R., 2012. Mass balance of pilot-scale pretreatment of sugarcane bagasse by steam explosion followed by alkaline delignification. Bioresour. Technol. 111, 447–452. https://doi.org/10.1016/j.biortech.2012.02.005
- Rosales-Calderon, O., Arantes, V., 2019. A review on commercial-scale high-value products that can be produced alongside cellulosic ethanol. Biotechnol. Biofuels 12, 1–58.

https://doi.org/10.1186/s13068-019-1529-1

- Sánchez, C., Serrano, L., Andres, M.A., Labidi, J., 2013. Furfural production from corn cobs autohydrolysis liquors by microwave technology. Ind. Crops Prod. 42, 513–519. https://doi.org/10.1016/j.indcrop.2012.06.042
- Schmidt, L.M., Mthembu, L.D., Reddy, P., Deenadayalu, N., Kaltschmitt, M., Smirnova, I., 2017. Levulinic acid production integrated into a sugarcane bagasse based biorefinery using thermal-enzymatic pretreatment. Ind. Crops Prod. 99, 172–178. https://doi.org/10.1016/j.indcrop.2017.02.010
- Shi, X., Zhao, B., Zhou, H., Tian, Y., Qiao, Y., Ji, B., 2019. Direct Saccharification and
   Fermentation for High Glucose and Ethanol Production from Non-Detoxified Furfural
   Residue Without Any Pretreatment. Energy Technol. Environ. Sci. 4, 7844–7850.

https://doi.org/10.1002/slct.201901367

Shinde, S.D., Meng, X., Kumar, R., Ragauskas, A.J., 2018. Recent advances in understanding the pseudo-lignin formation in a lignocellulosic biorefinery. Green Chem. 20, 2192– 2205. https://doi.org/10.1039/c8gc00353j

Silva, J.F.L., Selicani, M.A., Junqueira, T.L., Klein, B.C., Vaz, S., Bonomi, A., 2017. Integrated furfural and first generation bioethanol production: Process simulation and technoeconomic analysis. Brazilian J. Chem. Eng. 34, 623–634. https://doi.org/10.1590/0104-6632.20170343s20150643

- Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., Crocker, D., 2012. Determination of Structural Carbohydrates and Lignin in Biomass, National Renewable Energy Laboratory, Technical Report NREL/TP-510-42618, Revised August 2012.
- Smithers, J., 2014. Review of sugarcane trash recovery systems for energy cogeneration in South Africa. Renew. Sustain. Energy Rev. 32, 915–925. https://doi.org/10.1016/j.rser.2014.01.042
- Steinbach, D., Kruse, A., Sauer, J., 2017. Pretreatment technologies of lignocellulosic
   biomass in water in view of furfural and 5-hydroxymethylfurfural production- A review.
   Biomass Convers. Biorefinery. https://doi.org/10.1007/s13399-017-0243-0
- Sun, S.N., Cao, X.F., Li, M.F., Xu, F., Sun, R.C., 2013. Treatment of Furfural Residue by Solvent Extraction for Enzymatic Hydrolysis: Effect of Delignification on the Structure and Digestibility. Bioenergy Res. 6, 1022–1029. https://doi.org/10.1007/s12155-013-9329-0
- Tabatabaei, M., Mortaza, A., Valijanian, E., Panahi, H.K.S., Nizami, A.-S., Ghanavati, H., Sulaiman, A., Mirmohamadsadeghi, S., Karimi, K., 2020. A comprehensive review on recent biological innovations to improve biogas production, Part 1 : Upstream strategies. Renew. Energy 146, 1204–1220.

https://doi.org/https://doi.org/10.1016/j.renene.2019.07.037

- Unrean, P., Ketsub, N., 2018. Integrated lignocellulosic bioprocess for co-production of ethanol and xylitol from sugarcane bagasse. Ind. Crop. Prod. 123, 238–246.
- Unrean, P., Khajeeram, S., 2016. Optimization and techno-economic assessment of highsolid fed-batch sacchari fi cation and ethanol fermentation by Scheffersomyces stipitis and Saccharomyces cerevisiae consortium. Renew. Energy 99, 1062–1072. https://doi.org/10.1016/j.renene.2016.08.019
- Unrean, P., Khajeeram, S., Laoteng, K., 2016. Systematic optimization of fed-batch simultaneous saccharification and fermentation at high-solid loading based on enzymatic hydrolysis and dynamic metabolic modeling of Saccharomyces cerevisiae.
  Appl. Microbiol. Biotechnol. 100, 2459–2470. https://doi.org/10.1007/s00253-015-7173-1
- Uppal, S.K., Kaur, R., 2011. Hemicellulosic Furfural Production from Sugarcane Bagasse Using Different Acids. Sugar Tech 13, 166–169. https://doi.org/10.1007/s12355-011-0081-5
- Vallejos, M.E., Felissia, F.E., Kruyeniski, J., Area, M.C., 2015. Kinetic study of the extraction of hemicellulosic carbohydrates from sugarcane bagasse by hot water treatment. Ind.
   Crops Prod. 67, 1–6. https://doi.org/10.1016/j.indcrop.2014.12.058
- Vázquez, M., Oliva, M., Téllez-Luis, S.J., Ramírez, J.A., 2007. Hydrolysis of sorghum straw using phosphoric acid: Evaluation of furfural production. Bioresour. Technol. 98, 3053– 3060. https://doi.org/10.1016/j.biortech.2006.10.017
- Wang, K., Yang, H., Chen, Q., Sun, R. cang, 2013. Influence of delignification efficiency with alkaline peroxide on the digestibility of furfural residues for bioethanol production. Bioresour. Technol. 146, 208–214. https://doi.org/10.1016/j.biortech.2013.07.008

Wang, W., Ren, J., Li, H., Deng, A., Sun, R., 2015. Direct transformation of xylan-type

hemicelluloses to furfural via SnCl4 catalysts in aqueous and biphasic systems. Bioresour. Technol. 183, 188–194. https://doi.org/10.1016/j.biortech.2015.02.068

Wang, X., Fai, Y., Li, Y., Ma, X., Cui, S., Zhang, T., 2017. Inhibitory e ff ects of phenolic compounds of rice straw formed by sacchari fi cation during ethanol fermentation by Pichia stipitis. Bioresour. Technol. 244, 1059–1067.
https://doi.org/10.1016/j.biortech.2017.08.096

Wang, Z., Zhuge, J., Fang, H., Prior, B.A., 2001. Glycerol production by microbial fermentation : A review. Biotechnol. Adv. 19 19, 201–223. https://doi.org/10.1016/S0734-9750(01)00060-X

- Watanabe, K., Tachibana, S., Konishi, M., 2019. Modeling growth and fermentation inhibition during bioethanol production using component pro fi les obtained by performing comprehensive targeted and non-targeted analyses. Bioresour. Technol. 281, 260–268. https://doi.org/10.1016/j.biortech.2019.02.081
- Xing, R., Wei, Q., Huber, G.W., 2011. Production of furfural and carboxylic acids from waste aqueous hemicellulose solutions from the pulp and paper and cellulosic ethanol industries<sup>†</sup>. Energy Environ. Sci. 4, 2193–2205. https://doi.org/10.1039/c1ee01022k
- Xing, Y., Bu, L., Sun, D., Liu, Z., Liu, S., Jiang, J., 2016. Enhancement of high-solids enzymatic hydrolysis and fermentation of furfural residues by addition of Gleditsia saponin. FUEL 177, 142–147. https://doi.org/10.1016/j.fuel.2016.03.024
- Xu, K., Seo, Y., Li, J., Li, C., 2019. Resistance mechanisms and reprogramming of microorganisms for e ffi cient biore fi nery under multiple environmental stresses.
   Synth. Syst. Biotechnol. J. 4, 92–98. https://doi.org/10.1016/j.synbio.2019.02.003
- Xu, Y., Wang, D., 2017. Integrating starchy substrate into cellulosic ethanol production to boost ethanol titers and yields. Appl. Energy 195, 196–203.

https://doi.org/10.1016/j.apenergy.2017.03.035

- Yan, K., Wu, G., Lafleur, T., Jarvis, C., 2014. Production, properties and catalytic
   hydrogenation of furfural to fuel additives and value-added chemicals. Renew. Sustain.
   Energy Rev. 38, 663–676. https://doi.org/10.1016/j.rser.2014.07.003
- Yemiş, O., Mazza, G., 2012. Optimization of furfural and 5-hydroxymethylfurfural production from wheat straw by a microwave-assisted process. Bioresour. Technol. 109, 215–223. https://doi.org/10.1016/j.biortech.2012.01.031
- Yemiş, O., Mazza, G., 2011. Acid-catalyzed conversion of xylose, xylan and straw into furfural by microwave-assisted reaction. Bioresour. Technol. 102, 7371–7378. https://doi.org/10.1016/j.biortech.2011.04.050
- Yoo, C.G., Kuo, M., Kim, T.H., 2012. Ethanol and furfural production from corn stover using a hybrid fractionation process with zinc chloride and simultaneous saccharification and fermentation (SSF). Process Biochem. 47, 319–326. https://doi.org/10.1016/j.procbio.2011.11.018
- Zabed, H., Sahu, J.N., Suely, A., Boyce, A.N., Faruq, G., 2017. Bioethanol production from renewable sources: Current perspectives and technological progress. Renew. Sustain.
   Energy Rev. 71, 475–501. https://doi.org/10.1016/j.rser.2016.12.076
- Zang, G., Shah, A., Wan, C., 2020. Techno-economic analysis of an integrated biore fi nery strategy based on one-pot biomass fractionation and furfural production. J. Clean. Prod. 260, 120837. https://doi.org/10.1016/j.jclepro.2020.120837
- Zeitsch, K.J.J., 2000. The chemistry and technology of furfural and its many by-products, Sugar Series Vol. 13, Elsevier, The Netherlands. https://doi.org/10.1016/S1385-8947(00)00182-0

Zhang, L., Xi, G., Zhang, J., Yu, H., Wang, X., 2017. Efficient catalytic system for the direct

transformation of lignocellulosic biomass to furfural and 5-hydroxymethylfurfural. Bioresour. Technol. 224, 656–661. https://doi.org/10.1016/j.biortech.2016.11.097

Zhang, X., Bai, Y., Cao, X., Sun, R., 2017. Pretreatment of Eucalyptus in biphasic system for furfural production and accelerated enzymatic hydrolysis. Bioresour. Technol. 238, 1–6. https://doi.org/10.1016/j.biortech.2017.04.011

Zhao, M., Shi, D., Lu, X., Zong, H., Zhuge, B., Ji, H., 2019. Ethanol fermentation from nondetoxified lignocellulose hydrolysate by a multi-stress tolerant yeast Candida glycerinogenes mutant. Bioresour. Technol. 273, 634–640. https://doi.org/10.1016/j.biortech.2018.11.053

 Zhao, X., Liu, D., 2019. Multi-products co-production improves the economic feasibility of cellulosic ethanol : A case of Formiline pretreatment-based biore fi ning. Appl. Energy 250, 229–244. https://doi.org/10.1016/j.apenergy.2019.05.045

#### **Chapter 2: Literature review**

#### 2.1 Introduction

Sugarcane bagasse and harvest residues are lignocellulosic materials that consists of cellulose, hemicellulose and lignin arranged in a complex matrix structure leading to its recalcitrance, which ensures that its carbohydrates are protected against microbial and enzymatic hydrolysis and deconstruction (Mohlala et al., 2016; Smithers, 2014; Unrean and Khajeeram, 2016). The crystallinity, degree of polymerization of cellulose, accessible surface area, cellu-lignin structure, casing of cellulose by hemicellulose and fibre strengths affect the recalcitrance of lignocellulosic biomass (Boshoff et al., 2016; Cardona et al., 2010). Thus, lignocelluloses require pretreatment prior to biochemical conversion, as they do not contain readily available monomeric sugars. Pretreatment renders the biomass solids accessible to enzyme activity, which converts it to hexose and pentose sugars (mainly glucose and xylose) that are subsequently fermented using suitable microorganisms (Unrean and Ketsub, 2018; Watanabe et al., 2019). The conditions of pretreatment determine the extent of digestibility of cellulose and the amount of hemicellulose sugars recovered in the hydrolysate (Cardona et al., 2010; Steinbach et al., 2017).

The changes in chemical structure of the cellu-lignin matrix structure includes the deformation of bonds in C–O and C–H found in the polysaccharides and lignin, C=C found in lignin, and C–O found in the aromatic ring (Brienzo et al., 2017). The lignin matrix negatively affects the digestibility of cellulose as it is a structural barrier to enzyme binding (Brienzo et al., 2017; Sun et al., 2013). Ineffective enzyme binding leads to low yield of sugars that are needed for ethanol production. However, lower lignin content does not necessarily lead to

high yield of fermentable sugars (Sun et al., 2013). Likewise, morphological changes influence enzyme binding, since the solids needs to be porous and rigid to improve accessibility for enzymatic action (Sun et al., 2013). The crystallinity of the solid residues increases after pretreatment, because of the removal of the amorphous biomass component, primarily the arabinoxylan (Zhang et al., 2017). Apart from removal of amorphous material, cellulose with a low degree of polymerisation is preferred due to high content of individual celluloses exposed to enzymatic action (Brienzo et al., 2017). However, previous studies (Brienzo et al., 2017; Sun et al., 2013) show that there is no correlation between glucose yield and changes in crystallinity or degree of polymerization.

Pretreatment under severe conditions leads to increased formation of fermentation yeast inhibitors, which reduces ethanol yield (Cardona et al., 2010; Zabed et al., 2017). For instance, the use of acidic pretreatment techniques at harsh conditions lead to formation of furan derivatives and other unknown toxic products that need to be removed prior to the enzymatic hydrolysis, which adds to process costs (He et al., 2016; Mesa et al., 2014). Acetic and formic acids are also formed during acid pretreatment and have inhibitory effects during enzymatic hydrolysis. Furthermore, harsh conditions will also hydrolyse parts of the cellulose to hexose sugars, which will report to the hemicellulose hydrolysate and may be lost when fermentation only utilises the residual solids as feedstock. On the other hand, less harsh conditions will not effectively remove the hemicellulose attached to the cellulose. Liquid hot water pretreatment is less harsh and will result in inefficient removal of hemicellulose, but will not result in cellulose losses (Cardona et al., 2010; Steinbach et al., 2017). Recovery of solids generally decreases with an increase in combined severity (Mesa et al., 2017).
Harsh pretreatment conditions promote formation of furfural, whereas less severe pretreatment conditions produce pentose sugars, while preserving the cellulose for enzymatic hydrolysis (Cai et al., 2014). The pretreatment stage of cellulosic ethanol production is one of the major process costs (Cardona et al., 2010). Hence, the overall lignocellulosic ethanol process economics can be improved by co-production with furfural which is a high value (≥2200 US\$/tonne) biochemical that is applied as a solvent in the oil refinery, lubricant for pesticides and fungicides and used as a platform chemical (Cai et al., 2014; Moncada et al., 2016; Rosales-Calderon and Arantes, 2019).

## 2.2 Furfural production

Production of furfural at industrial scale was started in 1921 by the Quaker Oats Company (Cai et al., 2014; Zeitsch, 2000). The SupraYield and Single-step Continuous process, CIMV (Compagnie Industrielle de la Matière Végétale) and MTC (multi-turbine column) are amongst industrial processes employed for furfural production (Dashtban et al., 2012). The Quaker Oats company utilised oat hulls as feedstock whereas sugarcane bagasse, wheat straw and straw are used as feedstock by the SupraYield and single-step continuous process, CIMV and MTC, respectively. Feedstock with high hemicellulose content is desirable for furfural production, however, the selection of feedstock is also driven by availability and costs (Cai et al., 2014; Rosales-Calderon and Arantes, 2019)

Currently, the global annual production rate of furfural is about 270-300 ktonne with China being the main producer followed by the Dominican Republic and South Africa (Rosales-Calderon and Arantes, 2019). The low demand of furfural coupled with expensive plant

maintenance costs have hindered further development of furfural production methods and potential yield increases (Cai et al., 2014; Nhien et al., 2016). In addition, energy demands are high in the current commercial processes for furfural production (Nhien et al., 2016). Thus, production methods and furfural yield require improvements for furfural and its derivatives to survive market conditions (Cai et al., 2014; Rosales-Calderon and Arantes, 2019).

Furfural is only formed from pentosans contained in the hemicellulose portion of lignocellulosic biomass (Bamufleh et al., 2013; Vázquez et al., 2007; Zeitsch, 2000). Hemicellulose is made up of a complex group of polysaccharides such as xylan, glucuronoxylan, arabinoxylan, mannan, glucomannan and galactoglucomannan (Lin et al., 2017). The hemicelluloses that contain xylans are suitable for furfural production, which occurs through the hydrolysis and dehydration of pentosans and the resulting pentoses, respectively (Vázquez et al., 2007; Zeitsch, 2000). The digestibility and chemical properties of the cellulose components in resulting solids after furfural formation are altered rendering them more susceptible to enzymatic hydrolysis, because of hemicellulose removal although the lignin content is increased (Mesa et al., 2014). Thus, the furfural process can act as a pretreatment step for ethanol production (Cai et al., 2014; Mesa et al., 2014). Nevertheless, the cellulose fraction is degraded during furfural production at harsh conditions, thereby resulting in less amount of solids available for subsequent processes that use cellulose as raw material (Raman and Gnansounou, 2015).

Reactions 1 and 2 show the generic mechanism for hydrolysis and dehydration of pentosan and the resulting pentose to form furfural (Zeitsch, 2000). The maximum theoretical yields of furfural from pentosans and pentoses are 72.73% and 64.00% by weight, respectively

(Zeitsch, 2000). Furfural formation is usually aided by either an acidic homogenous or heterogeneous catalyst (Bamufleh et al., 2013; Danon et al., 2013; Dashtban et al., 2012).

$$(C_5 H_8 O_4)_n + n H_2 O \to n(C_5 H_{10} O_5)$$
 Reaction 1

$$C_5H_{10}O_5 \rightarrow C_5H_4O_2 + 3H_2O$$
 Reaction 2

There are four main systems employed for the production of furfural namely the autocatalytic, aqueous-acid catalytic, bi-phasic systems (Zhang et al., 2014) and the solid catalytic/bi-phasic systems (Dashtban et al., 2012). There is no external catalyst added in the autocatalytic systems, the acetyl groups liberated from biomass act as catalysts (Dashtban et al., 2012; Sánchez et al., 2013). In the aqueous-acid systems, sulphuric acid, nitric acid, hydrochloric acid, phosphoric acid and formic acid are some of the commonly used acids (Dashtban et al., 2012). The bi-phasic systems consist of a mixture of an organic and aqueous phase making up the reaction media (Xing et al., 2011). Lastly, solid catalysts such as zeolites and silicoaluminophosphates are usually compatible with all common solvents (Bruce et al., 2016; Ghosh et al., 2015).

All furfural production configurations operate either as a one-stage (direct method) or two-stage processes (indirect method) (Dashtban et al., 2012). In the one-stage process, both hydrolysis and dehydration occur in a single unit, whereas hydrolysis and dehydration occur in separate units with solid-liquid separation after hydrolysis when the two-stage furfural method is employed (Dashtban et al., 2012).

## **2.3 Furfural production methods**

## 2.3.1 One-stage furfural production (Direct furfural method)

The one-stage furfural production from lignocellulosic biomass has been demonstrated in several studies (Avci et al., 2013; Dussan et al., 2013; Zhang et al., 2017). In the one-stage furfural method (shown in Figure 2.1a), the hemicellulose component of biomass is hydrolysed to its sugars, which are subsequently converted to furfural in the same reactor vessel, operated at severe conditions. The main process variables are catalyst concentrations, temperature and time, which are varied such that the severity is sufficient to form furfural in one stage (Avci et al., 2013; Dussan et al., 2013; Zhang et al., 2017). However, industrial furfural residues tend to have high contents of lignin (67 w/w%) due to cellulose degradation (Mesa et al., 2014). The types of biomass used as feedstock in these studies include sugarcane bagasse, corncobs, corn stover, switchgrass, midribs of date-palm trees, miscanthus, eucalyptus, sorghum straw, corn stover and aspen strands as well as Mixed Northern Hardwoods with corncobs being the most common (Mao et al., 2012; Li et al., 2016; Sánchez et al., 2013; Wang et al., 2017; Xing et al., 2011).

Solvents are required in the production of furfural and the most common type of solvent used is water (Wang et al., 2017; Avci et al., 2013; Dussan et al., 2013; Vazquez et al., 2007; Bamufleh et al., 2013). Organic solvents such as toluene, acetic acid and gamma-valerolactone (GVL) are sometimes added to furfural production process to minimise furfural degradation reactions that are faster in the aqueous phase (Abad et al., 1997; Bruce et al., 2016).

Biphasic systems are used to reduce process operational costs associated with distillation, for instance, energy requirements are reduced when organic solvents having

lower boiling points are used (Cai et al., 2014). However, the necessary recycling of solvents is expensive, the solvents are costly, and they introduce safety hazards under furfural process conditions (Cai et al., 2014). Moreover, the use of toxic solvents makes the biobased chemical production process ineffective, due to the negative environmental impacts caused by these (Cai et al., 2014; Farzad et al., 2017). In contrast, the use of water as a solvent does not introduce any additional process units for recovery and recycling purposes.

Furfural processes that employ water as a solvent with no additional catalyst are known as autocatalytic processes, although acid catalysts are usually introduced to speed up the furfural formation reaction (Steinbach et al., 2017). External homogenous catalysts usually introduced into the process include dilute sulphuric acid (Dussan et al., 2013; Yemis and Mazza, 2011), nitric acid (Uppal and Kaur, 2011; Yemis and Mazza, 2012), phosphoric acid (Vazquez et al., 2007; Wang et al., 2017) and hydrochloric acid (Abad et al., 1997; Xing et al., 2011). Formic and acetic acid are also used as homogeneous organic acid catalysts (Mao et al., 2012; Uppal and Kaur, 2011).

Utilization of sulphuric acid for hydrolysis leads to a more cost-effective furfural production processes since there is no acid recycling required and it is relatively cheap compared to other acids (Steinbach et al., 2017). Hydrochloric acid poses safety risks due to its volatility and is more likely to corrode process equipment (Steinbach et al., 2017). Phosphoric acid is a weaker acid compared to sulphuric acid, thus, larger amounts of phosphoric acid will be required to achieve higher yields. Yemis and Mazza (2011) investigated the influence of type of acidic-catalyst on furfural yield from xylan. The acid catalysts compared were sulphuric, nitric, phosphoric, hydrochloric, formic and acetic and the highest furfural yield from xylan was obtained when hydrochloric acid was used. Interestingly,

the second highest furfural yield was obtained when sulphuric acid was used with a difference of less than 20% in terms of yield (Yemiş and Mazza, 2012, 2011).

Besides homogenous catalyst, heterogeneous catalyst are also used in one-stage furfural production processes; however, the catalyst separation techniques from the solids residue are not discussed in the reviewed studies and solid-solid separation requires an additional process unit performing separation based on size or density (Bruce et al., 2016). Solid catalysts that have been studied include silicoaluminophosphates (SAPO) (Bruce et al., 2016), ZSM-5 zeolite, SO<sub>4</sub><sup>2-</sup>/SiO<sub>2</sub>-AlO<sub>2</sub>O<sub>3</sub>/La<sup>3+</sup> (Wang et al., 2015) and Aluminium-Beta (Zhang et al., 2017). Solid acid catalysts do not cause corrosion to process equipment and can be easily separated from liquid phase, and are thus more suitable for the two-stage method (Deng et al., 2016). However, solid acid catalysts require regeneration for continued efficient operation. Despite their advantages, regeneration steps will increase capital and operational costs due to the necessary regeneration unit and reagents.

The measured yield of furfural obtained from the one-stage production method ranges from 15 to 83% of the theoretical maximum, as tabulated in Table 2.1, with an average yield of 59%. The highest yield of 83 % of the theoretical maximum was obtained when a solid catalyst was used at a temperature of 190°C after combined ball milling and ultrasonic pretreatment of the lignocellulose. Longer residence times increased the yield of furfural at lower temperatures when weaker acids were used as catalysts (Uppal and Kaur, 2011; Vázquez et al., 2007). Conversely, similar yields were obtained within a shorter residence time at elevated temperatures ( $\geq$ 180°C) in systems that utilised strong acids (HCl, H<sub>2</sub>SO<sub>4</sub>) (Table 2.1). At the highest solids loading of about 60%, the furfural yield was 68%. To reach this yield at high solids loading, biomass was packed in a reactor (180°C) and steam was injected with FeCl<sub>3</sub> and acetic acid as co-catalysts and the formed furfural was continuously extracted (Mao

et al., 2012). Generally, furfural yield increases with an increase in temperature, residence time and acid concentration, whilst it decreases with an increase in solids loading percentage due to reduced mass transfer (Bamufleh et al., 2013; Vazquez et al., 2007; Yemis and Mazza, 2011).

Furfural yields (as % of theoretical yield) from one-stage furfural obtained in coproduction with ethanol were 53 % (Mesa et al., 2014) and 62 % (Avci et al., 2013) from sugarcane bagasse and corn stover, respectively, at lab scale of up to one gram of substrate per 10 to 20 mL of solvent (water). Furfural yield obtained by Mesa et al. (2014) is below the average of 57% due to differences in extent of furfural formation and degradation reactions driven by process severity. The longer residence time of 40 minutes employed by Mesa et al. (2014), led to larger losses of furfural via degradation reactions as compared to 20 minutes employed by Avci et al. (2013). Noteworthy, Mesa et al. (2014) produced furfural using a stronger acid catalyst in higher concentration (1.25 wt% H<sub>2</sub>SO<sub>4</sub>) as compared to Avci et al. (2013) (0.75 wt% H<sub>3</sub>PO<sub>4</sub>). Although Avci et al. (2013) operated at a higher temperature (200°C), the weaker acid together with shorter residence time reduced the extent of furfural degradation reactions. Moreover, the low solids loading of 5% employed by Avci et al. (2013) also promoted furfural formation because of improved mass and heat transfer. Studies also shows that increasing scale can reduce yield by about 15-20% as demonstrated differences in furfural yields at small scale (57%) and bench scale (35%) due to differences in mass and heat transfer at different scale of operation and set-up (Mesa et al., 2014).

Biomass	S/L	Solvent	Catalyst	T (°C)	time (min)	yield %	yield (g/kg)	Reference
Eucalyptus globulus	1 g to 10 mL	H <sub>2</sub> O-AcOH (5:95%)	HCI (0.4% w/w)	130	45	not stated	45	Abad et al., 1997
Sorghum straw	1 g to 10 mL	H <sub>2</sub> O	H₃PO₄ (6 wt %)	134	300	78	137	Vazquez et al., 2007
Date-palm midribs	1 g to 50 mL	H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> (5-15 %w/w)	140	30	32	56	Bamufleh et al., 2013
Miscanthus	1 g to 10 mL	H <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub> (0.526 M)	150	±100	53	45	Dussan et al., 2013
Wheat straw	1 g to 100 mL	H <sub>2</sub> O	0.1 M HCI	180	20	not stated	104	Yemiş & Mazza, 2011
Triticate straw	1 g to 100 mL	H <sub>2</sub> O	0.1 M HCI	180	20	not stated	109	Yemiş & Mazza, 2011
Flax shives	1 g to 100 mL	H <sub>2</sub> O	0.1 M HCI	180	20	not stated	102	Yemiş & Mazza, 2011
Sugarcane bagasse	1 g to 15 mL	H <sub>2</sub> O	3 M HNO3	110	300	not stated	120	Uppal and Kaur, 2011
Corncob	1 g to 0.6 g (steam reactor)	H <sub>2</sub> O	20mM FeCl <sub>3</sub> , 3%acetic acid	180	30	68	158	Mao et al., 2012
Corncob	1 g to 8 mL	H <sub>2</sub> O	Autohydrolysis	180	30	15	32	Sánchez et al., 2013
Corncob	1 g to 8 mL	H <sub>2</sub> O	0.5 -3% v/v H <sub>2</sub> SO <sub>4</sub>	180	30	48	105	Sánchez et al., 2013
Corncob	1 g to 8 mL	H <sub>2</sub> O	0.5 -3% v/v HCl	180	30	51	111	Sánchez et al., 2013
Corncob	1 g to 41 mL	Gamma valerolactone	FeCl <sub>3</sub> 6H <sub>2</sub> O	185	100	80	146	Zhang et al., 2014
Corncob	1 g to 20 mL	H <sub>2</sub> O	Solid SO4 <sup>2-</sup> /SiO <sup>2-</sup> AlO2O3/La <sup>3+</sup>	190	30	83	198	Li et al., 2016
Switchgrass	1 g to 49 mL	90% Gamma- valerolactone, 10% H <sub>2</sub> O	SAPO A70	190	24	61	174	Bruce et al., 2016
Sugarcane bagasse	1g to 10 mL	H <sub>2</sub> O	1.25 %w/w H <sub>2</sub> SO <sub>4</sub>	175	40	53	91	*Mesa et al., 2014
Corn stover	1g to 20 mL	H <sub>2</sub> O	0.75 % (v/v) H₃PO₄	200	20	62	108	*Avci et al., 2013

## Table 2. 1: Summary of furfural production from biomass studies using the one-stage method.

Note: \*Furfural co-produced with ethanol from the cellu-lignin residues, obtained from the furfural process; % yield is expressed as percentage of theoretical yield.

## 2.3.2 Two-stage furfural production (Indirect furfural method)

The two-stage furfural production method (shown in Figure 2.1b) starts with a pretreatment step that aims to produce a hydrolysate composed mainly of pentose sugars particularly xylose, and this separates the cellu-lignin from hemicellulose component of lignocellulose (Steinbach et al., 2017). Pretreatment of lignocellulose materials also increases the accessible surface area, changes the lignin structure and removes lignin when alkaline pretreatment is employed (Cardona et al., 2010). Amongst the techniques used for biomass pretreatment to generate a hemicellulose hydrolysate for furfural production, are steam explosion, liquid hot water, dilute acid as well as alkali treatment (Moncada et al., 2016; Chen et al., 2015). Steam explosion, liquid hot water and dilute acid pretreatment methods remove the hemicelluloses leaving an altered cellu-lignin structure that is characterised with higher digestibility and increased accessible surface area compared to untreated biomass (Steinbach et al., 2017).

Steam explosion operation is an inexpensive method for pretreatment, since it can be conducted without addition of a catalyst (Chen et al., 2015; Steinbach et al., 2017). Furthermore, the resulting sugars from steam explosion are less diluted (Steinbach et al., 2017). Likewise, liquid hot water treatment requires no additional catalysts and minimizes the amount of chemicals needed for downstream process conditioning (Steinbach et al., 2017). To enhance efficiency of acid pretreatment, zinc chloride may be added into the first stage (Yoo et al., 2012). Zinc chloride is an inorganic swelling agent with a higher selectivity for hemicellulose hydrolysis and forms zinc-cellulose complexes capable of undergoing hydrolysis leading to cellulose characterised with a low-degree of polymerisation (Yoo et al., 2012). The

addition of zinc chloride increases process operating costs and requires a water treatment system capable of removing zinc and chlorine ions.

Similar to the one-stage method, water and organic solvents are also used in the twostage furfural production systems. Organic solvents that have been used in the two-stage method studies include methyl isobutyl ketone (Ghosh et al., 2015) and dichloromethane (Deng et al., 2016). The rationale for using water-immiscible solvents is to ensure that furfural is immediately extracted into the organic phase after formation, to minimize the furfural degradation that occurs in the aqueous phase (Deng et al., 2016).

Both homogeneous and heterogeneous catalysts have been employed in the twostage production of furfural. Comparable to the one-stage method, sulphuric acid and hydrochloric acid are used as catalysts in the two-stage furfural production. When homogenous catalysts are used, the catalyst is added to both the first and second stage of two-stage furfural process (Moncada et al., 2016). However, catalyst is not always added in the second stage, provided the hydrolysate contains sufficient acid to catalyse the dehydration of the pentose sugars (Raman and Gnansounou, 2015). Adding more acid to the process will create harsh conditions that lead to furfural loss via resinification and/or condensation (Raman and Gnansounou, 2015).

Besides acid catalysts, alkaline catalysts such as sodium hydroxide are also used in the pretreatment stage of the two-stage furfural production. In comparison to sulphuric acid and hot water pretreatment, sodium hydroxide produced the highest yield of sugars and concentration (Moncada et al., 2016). However, the second stage required sulphuric acid as catalyst to produce furfural (Moncada et al., 2016). Sulphuric acid consumption will be higher when pretreatment is conducted in alkaline medium, as the acid must first neutralise the

alkali used prior to creating acidic conditions within the hydrolysate to induce xylose conversion to furfural.

Solid catalysts have also been employed in the second stage for two-stage furfural production (Deng et al., 2016; Ghosh et al., 2015; Chen et al., 2015). The solid catalysts used are the Indion solid catalyst (Ghosh et al., 2015), HZMS-5 catalyst (Chen et al., 2015) and biochar catalysts made from corncob, which was also the process feedstock (Deng et al., 2016). All the solid catalysts used in the second stage are acidic in nature (Deng et al., 2016; Ghosh et al., 2015). As stated in the previous section, solid catalysts are easily separated from liquid phase, however, regeneration steps increase capital and operational costs.

The yield of furfural from the two-stage method based on initial biomass ranges from 48 to 91 % of the theoretical furfural yield with an average of 77 % as tabulated in Table 2.2. The maximum furfural yield of 91% obtained was obtained in different studies during coproduction with ethanol at different furfural operating conditions (residence time and temperatures) using different catalysts having different concentrations (Moncada et al., 2016; Yoo et al., 2012; Raman and Gnansounou, 2015). However, Moncada et al. (2016) utilised sodium hydroxide as a pretreatment reagent, which potentially increased acid consumption in the dehydration step due to the hydroxyl ions from the pretreatment step. The lowest furfural yield of 59% achieved was under co-production with ethanol when a solid catalyst was used. The lower yield is attributed to furfural degradation reactions induced by the highly acidic conditions in the furfural stage due to the combination of hydrogen ions from the pretreatment stage and the additional acidic solid catalyst (Ghosh et al., 2015). Amongst the reviewed two-stage furfural production studies, the lowest furfural yield (48%) was obtained when steam explosion was used as a pretreatment technique (Chen et al., 2015). The use of

steam explosion resulted in a pentose sugar concentration of about 0.52 g/L (~0.05 wt %) as compared to at least 23 g/L (~2.38 wt %) of pentose in other studies. In most studies focussed on co-production of ethanol and furfural using the two-stage method do not utilise the furfural vapour releasing reactor, which minimises furfural degradation while concentrating furfural prior to purification and recovery by distillation (Zeitsch, 2000; Mao et al., 2012; Cai et al., 2014). Table 2. 2: Summary of furfural production from biomass studies using the two-stage method.

Biomass	Pretreatment (1 <sup>st</sup> stage)	[Xylose]	Catalyst	Solvent	T (°C)	t (min)	Furfural yield % <sup>a</sup>	Furfural yield <sup>ь</sup> (g/kg)	Reference
Corncob	oxalic acid assisted	5 wt%	Biochar	Methyl Isobutyl	170	60	81	183	Deng et al., 2016
	ball milling at 190°C			ketone					
	for 60 min								
Sugarcane	0.25v/v H <sub>2</sub> SO <sub>4</sub> (120-	37g/L	30% w/w	Dichloromethan	170	60	59	112	*Ghosh et al., 2015
bagasse	140ºC), 90 to 180	(~3.7%)	Indion 130	е					
	min								
Corn stover	0.03 wt% HCI + 5%	Not given	No	H <sub>2</sub> O	150	120	91	102	*Yoo et al., 2012
	ZnCl <sub>2</sub> , 150 °C for 10		additional						
	min, 170°C for 10		catalyst						
	min								
Dried oil palm,	1.025%v/v H <sub>2</sub> SO <sub>4</sub> at	23.8 g/L	No	H <sub>2</sub> O	198	11	91	57	*Raman &
Empty fruit	160 °C for 11 min	(2.38%)	additional						Gnansounou, 2015
bunch			catalyst						
Pinus patula	1% v/v NaOH at	40-120g/L	8 g/L	H <sub>2</sub> O	150	240	91	159	*Moncada et al., 2016
bark	121°C for 60 min	(4-12%)	$H_2SO_4$						
Rice straw	Steam explosion	0.52 g/L	HZSM-5	H <sub>2</sub> O	160	140	48	30	Chen et al., 2015
	200ºC, 1.5 MPa for 6	(0.05%)							
	min								

\*Furfural co-produced with ethanol

<sup>a</sup> Furfural yield expressed a percentage of theoretical yield

<sup>b</sup> Furfural yield based on mass of initial biomass

## 2.4 Ethanol production from lignocellulosic biomass

Generally, cellulosic ethanol production entails pretreatment, cellulose hydrolysis, fermentation, distillation and waste treatment (Cardona et al., 2010). Ethanol production from lignocellulosic material requires a pretreatment step to improve digestibility of the biomass prior to fermentation (Cardona et al., 2010). In the cellulose hydrolysis step, cellulose is converted into glucose sugars, which subsequently undergo fermentation in the next step. Thereafter, ethanol recovery and purification by distillation is conducted to reach the required market product specifications. Lastly, the effluent streams are treated to prevent release of harmful substances into the environment. In cases where pentose sugars are also fermented, a detoxification step is usually carried out to limit the extent of fermentation inhibitors (Cardona et al., 2010).

Ethanol production from lignocellulosic material is favoured as most of these materials are non-edible and are thus regarded as waste (Bezerra and Ragauskas, 2016). Therefore, there is no food security risk posed by lignocellulosic ethanol production (Cardona et al., 2010). Cellulosic bioethanol production at commercial scale is still challenging and there are few commercial plants in operation (Cardona et al., 2010; Xu and Wang, 2017; Jin et al., 2019). This is because the required enzymes are expensive, high water consumption, low ethanol concentration and low ethanol yield (Xu and Wang, 2017). Another contributor to the excessive costs of cellulosic ethanol is the pretreatment step (Xu and Wang, 2017; Cardona et al., 2010).

The main processing routes used for ethanol production from lignocellulose materials are Simultaneous Saccharification and Fermentation (SSF) and Separate Hydrolysis and Fermentation (SHF) (Katsimpouras et al., 2017; Nguyen et al., 2016). The major advantages of

SHF are the ability to operate both hydrolysis and fermentation at their respective optimum temperature and pH as well as ease of culture broth recycling (Nguyen et al., 2016). Advantages of the SSF process include minimization of inhibitors on enzymes since released sugars by hydrolysis are immediately fermented (Nguyen et al., 2016). Furthermore, the SSF is associated with low capital costs and minimal contaminants of the final ethanol product (Nguyen et al., 2016).

## 2.5 Sole production of ethanol, or its co-production with furfural

Dilute sulphuric acid is often used as a pretreatment catalyst for cellulosic ethanol production (Jeon et al., 2010; Patel et al., 2017). The dilute acid pretreatment step at elevated temperatures has some similarities to the one-stage furfural production method. Pretreatment of lignocellulosic biomass results in formation of xylose, furan derivatives and other unknown (potentially harmful) substances (Cardona et al., 2010). Other acids used include HCl, HNO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub>. Other pretreatment methods include alkaline pretreatment which mainly digest the lignin matrix (He et al., 2016; Xing et al., 2016). Other pretreatment techniques are thermal pretreatment, steam explosion, biological treatment, wet oxidation and *organolv* pretreatment (Cardona et al., 2010). An extensive review of pretreatment methods prior to fermentation has been outlined by Cardona et al. (2010). The pretreatment step renders the cellulose accessible to enzyme activity that further converts it to hexose sugars through hydrolysis (mainly glucose) that are fermented using a selected microbial strain (Unrean et al., 2016).

Fermentation efficiency also depends on the type of microbial strain utilised for the conversion of sugars to ethanol. The most frequently used fermentation microorganisms for

lignocellulosic ethanol production are the *Saccharomyces cerevisiae* (Katsimpouras et al., 2017; Patel et al., 2017; Nguyen et al., 2016). Conventional *S. cerevisiae* yeast only ferments hexose sugars (Cardona et al., 2010) and genetically modified or recombinant strains of *S. cerevisiae* are able to ferment both xylose and glucose (Mokomele et al., 2018; Watanabe et al., 2019). Other microorganisms that have been previously used for lignocellulose biomass fermentation with capability to ferment pentose sugars as well are *Escherichia coli* (Geddes et al., 2013) and *Zymomonas mobilis* (Jeon et al., 2010; Cardona et al., 2010). The extent of fermentation by the selected microbial strain determines the resulting ethanol yield (Cardona et al., 2010).

Sole ethanol production yields from acid pretreated bagasse using SHF and SSF ranges are 71-87% and 77-85%, respectively, as tabulated in Table 2.3. Overall, the resulting concentrations of ethanol are higher when SSF is employed as compared to SHF (Table 2.3). The use of higher solids loading in SSF results in higher ethanol concentrations (>50g/L) which decreases distillation costs (Cardona et al., 2010). In addition, the sugars released during SSF are fermented as they are produced thereby limiting their inhibitory effects on enzymes (Unrean et al., 2016). Ethanol yields may be further increased by introducing a delignification step, i.e., alkaline pretreatment, organosolv pretreatment, etc., prior to fermentation (Cardona et al., 2010), however, the introduction of an additional processing stage prior to fermentation increases the overall capital and operating costs.

The yield of ethanol when co-produced from the solids residues after furfural production, ranges from 46 to 99% as found in published data, and SHF is the commonly used fermentation strategy (Moncada et al., 2016; Raman and Gnansounou, 2015; Ghosh et al., 2015; Mesa et al., 2014; Avci et al., 2012). There was minimal cellulose degradation and

formation of inhibitors in the study where 99% ethanol yield was achieved, due to the use of a weaker acid (H<sub>3</sub>PO<sub>4</sub>) for furfural production and more importantly, the solids were detoxified through washing using water prior to fermentation (Avci et al., 2013). The range of ethanol yields when co-produced with furfural is wider than when produced alone, due to conditions employed for furfural production that affect the attainable ethanol yield from the resulting cellu-lignin solids. Under co-production with furfural, fermentation by the SSF strategy resulted in ethanol concentration of 17 g/L (22 g/100g of dry feedstock) as compared to 42 g/L (13 g/100g of dry feedstock) obtained under SHF due to the use of low solids loading (3%) to keep the concentration of inhibitors low, which led to a diluted ethanol product (Yoo et al., 2012). However, the yield of ethanol produced by SSF was up to 98% when co-produced with furfural (Yoo et al., 2012). Ethanol yields from the solid residues after one-stage furfural production, range from 87-99%, while for the residues after two-stage furfural production the range was 46-98%, as per Table 2.3.

The use of SSF at high solids loadings is generally the preferred technique for the fermentation of industrial furfural residues to obtain high ethanol yields and concentrations (Bu et al., 2014; He et al., 2016; Wang et al., 2013). Typically, corncob furfural residues blended with virgin lignocellulosic biomass are utilised as feedstock to improve ethanol yield (Wang et al., 2013; Xing et al., 2016; Bu et al., 2014; Ji et al., 2016). However, delignification by contacting with an alkaline or other reagent is employed as a pretreatment technique in most of these studies.

Generally, ethanol production from industrial furfural residue involves a delignification step to minimize enzyme inhibition by lignin (H. Ji et al., 2016) and the yield is about 75% of the theoretical yield (see Table 2.3). The ethanol concentration increased with

an increase in cellulose loading as tabulated in Table 2.3. The highest ethanol concentration reached from fermentation of furfural residues was 69.1 g/L at 20% solids loading (Xing et al., 2016). However, the cellulase loading was high (30 FPU/g) and multiple reagents (alkaline peroxide and gleditsia saponin) were used to pretreat the residues (Xing et al., 2016). Whereas, removal of inhibitors by washing and drying of industrial furfural residue without any other pretreatment resulted in an ethanol concentration of 37.6 g/L (He et al., 2016).

### 2.6 Integration of furfural and ethanol production

The co-production of furfural and ethanol in a biorefinery (shown in Figure 2.1) as a means for efficient utilization of lignocellulosic biomass such as sugarcane bagasse (Mesa et al., 2014; Ghosh et al., 2015), corn stover (Avci et al., 2013; Yoo et al., 2012), dried oil palm empty fruit bunch (Raman and Gnansounou, 2015) and *Pinus patula* bark (Moncada et al., 2016) has been investigated in several studies. The biorefinery approach offers advantages of valorising all the components of the lignocellulose material including energy production from lignin (Mesa et al., 2014; Ghosh et al., 2015; Moncada et al., 2016). In these studies, the performance of the one-stage and two-stage furfural methods in a biorefinery system have not been technically and economically compared to each other, especially not for the same batch of biomass substrate, thus, making it difficult to select the most suitable furfural production method. Instead, the techno-economic analysis was only conducted at a single set of process conditions (time, temperature and reagent concentration) and the process costs differed due to the various levels of energy integration in the scenarios considered and costing methods employed (Moncada et al., 2016).

The use of strong acidic catalysts to produce furfural using the one-stage method resulted in lower yields of both furfural and ethanol, due to furfural degradation and

degradation of the cellulose structure as well as formation of inhibitors that negatively affect fermentation of the cellu-lignin (Avci et al., 2013). For instance, furfural and ethanol yields were 61% and >92%, respectively, when  $H_3PO_4$  was used as compared to the use of  $H_2SO_4$ , which resulted in furfural and ethanol yield of 53% and 87%, respectively, as tabulated in Table 2.4. Furfural production occurs in acidic conditions that are somewhat similar to pretreatment conditions in ethanol production (Cai et al., 2014).

Nevertheless, ethanol and furfural co-production using the two-stage furfural method by means of acid pretreatment may achieve high yields of both ethanol and furfural in amounts of 91% and up to 98%, respectively (Table 2.4). Normally, the pretreatment stage of the two-stage furfural method is less harsh as it aims to convert hemicellulose into a hydrolysate composed mainly of xylose rather than producing furfural and as a result, the solid residues are degraded but more digestible (Steinbach et al., 2017). The pretreatment stage in the two-stage furfural production method increases capital cost due to the additional vessel required (Ghosh et al., 2015). Lastly, as in the one-stage furfural method, lower ethanol yield (61%) results when harsh conditions are employed in the pretreatment stage of the coproduction of ethanol and furfural employing two-stage method (Raman and Gnansounou, 2015).

Overall, as tabulated in Table 2.4, furfural yield achieved during co-production with ethanol is higher for two-stage furfural method as compared to the one-stage furfural method. The two-stage furfural method permits the use of optimal conditions for furfural formation, whereas the use of furfural optimal conditions in the one-stage furfural method reduces the yield of ethanol because of formation of inhibitors and cellulose degradation (Avci et al., 2013; Raman and Gnansounou, 2015). Generally, furfural yield is not maximised

under the co-production of ethanol and furfural using the one-stage method to ensure the furfural residues give higher ethanol yields (Mesa et al., 2014; Avci et al., 2013). Both furfural and ethanol yield can be potentially maximised when the two-stage furfural method is used, however, the yield of hemicellulose sugars from pretreatment and glucose from enzymatic hydrolysis are dependent on pretreatment conditions (Moncada et al., 2016; Cardona et al., 2010). Thus, the overall two-stage furfural and ethanol co-production method is limited by pretreatment conditions that determine whether hemicellulose sugars yield is maximised or glucose yield from enzymatic hydrolysis is maximised and vice versa.

Other challenges associated with co-production of ethanol and furfural include loss of furfural or pentose to cellulose filter cake, during its separation for liquid products, and high furfural recovery costs due to energy demands (de Jong and Marcotullio, 2010). Solids loading of 10% is usually used in the pretreatment stage, but it results in low concentrations of furfural (de Jong and Marcotullio, 2010). Using higher solids loadings potentially increase furfural concentration, although expensive process units compatible with high solids loading at the process temperatures and pressures will be required (de Jong and Marcotullio, 2010).

There are various process configurations for the co-production of ethanol and furfural as tabulated in Table 2.4. However, there are few studies in which an economic assessment has been conducted (Moncada et al., 2016; Farzad et al., 2017). These studies do not outline how the process economics vary at different process conditions and configurations implying that the explored conditions and configurations may not be economically optimised. Under optimal conditions, Moncada et al. (2016) employed alkaline pretreatment followed by twostage furfural production using acid, whereas Farzad et al. (2017) utilised steam explosion pretreatment prior to dehydration of sugars forming furfural. In the study by Moncada et al.

(2016), the pretreated solids were washed prior to enzymatic hydrolysis and fermentation. The pretreated solids were not washed in the process configurations considered Farzad et al. (2017) to prevent additional costs associated with additional process units and reagents, although organic solvents were employed for furfural separation and were found to increase operational costs and environmental burdens.

Farzad et al. (2017) and Moncada et al. (2016) reported an IRR and NPV of 7,5 % and 184,54 million US dollars, respectively (Table 2.5). The economic indicators used by Farzad et al. (2017) and Moncada et al. (2016) are different, thus, the process economics in the studies cannot be easily compared. Most techno-economic studies (Farzad et al., 2017; Hossain et al., 2019; Zang et al., 2020) focus on furfural and ethanol processes that include the use of organic solvents for furfural recovery, which causes environmental burdens.

Table 2.3	: Production of	f ethanol from	n virgin sugarcan	e bagasse and <sup>•</sup>	furfural residues.

Feed	Fermentation	Pretreatment	Microbial strain	Cellulase	yield <sup>t</sup>	Ethanol	Reference
	Method	method		loading	(%)	(g/L)	
SB	SHF	2% (v/v) H <sub>2</sub> SO <sub>4</sub>	Zymomonas mobilis ZM4	2%	71	10.3	Jeon et al., 2010
	(cofermentation)		(pZB5)	cellulase			
SB	SHF,Cell-	1.5% v/v H <sub>3</sub> PO <sub>4</sub>	S. cerevisiae Pe-2	15 FPU/g	87	49-52	Silva et al., 2015
	recycling						
SB	SHF-fed batch	1% v/w H <sub>2</sub> SO <sub>4</sub>	industrial strain of S-	15 FPU/g	79	~22	da Silva Martins et
			cerevisiae				al., 2015
SB	SHF,	1.5% H <sub>2</sub> SO <sub>4</sub>	S. Cerevisiae NCIM 3521 &	4-12	85	9.56	Patel et al., 2017
	cofermentation	+2% NaOH	Pichia Stipitis NCIM 3506	FPU/g			
SB	SSF (10%	1.5% H2SO4	S. cerevisiae	15 FPU/g	85	65	Unrean et al.,
	solids)						2016
SB	SSF/SHF (20%	Formic acid +	S. cerevisiae CICC 31014	15 FPU/g	77-81	55-80	Zhao and Liu,
	solids)	NaOH					2012
SB	SSF + (CELF)	(CELF)	S. cerevisiae D5A yeast	15 FPU/g	80	>50 g/L	Nguyen et al.,
	(11% solids)						2016
Industrial	SSF (10%	Water rinsed	S. cerevisiae (dry yeast)	7.5-30	77	19.3	He et al., 2016
FR	solids)			FPU /g			
Industrial	SSF-Fed batch	Water rinsed	S. cerevisiae (dry yeast & heat	15 FPU/g	75	37.6	He et al., 2016
FR	(10% solids)		tolerant)				
Industrial	SSF (5.5%	NaOH + H <sub>2</sub> O <sub>2</sub>	S. cerevisiae (dry yeast & heat	5 FPU/g	76-87	16.9	Wang et al., 2013
FR	solids)		tolerant)				
Industrial	SSF (20%	NaOH + GS	S. cerevisiae (dry yeast & heat	30 FPU/g	76	69.1	Xing et al., 2016
FR	solids)		tolerant)				
Industrial	SSF (5% solids)	NaOH + $H_2O_2$	S. cerevisiae (dry yeast & heat	12 FPU/g	76	not	Bu et al., 2014
FR			tolerant)			stated	
FR,	SSF (3% solids)	Water rinse	S. cerevisiae ATCC 200062	15 FPU/g	69-98	17	Yoo et al., 2012
indirect							
FR,	SHF	Enzymatic	Kluyveromyces sp. IIPE453	9 w/w %	88	17.1	Ghosh et al., 2015
indirect		saccharification		enzymes			
FR,	SHF	Enzymatic	S. cerevisiae no.1701	15 FPU/g	87	not	Mesa et al., 2014
direct		saccharification				stated	
FR,	SHF	Enzymatic	S. cerevisiae NRRL- Y2034	15 FPU/g	92-99	42	Avci et al., 2013
direct		saccharification					
FR,	SHF	Enzymatic	S. cerevisiae BY4741	10 FPU/g	46-61	not	Raman and
indirect		saccharification				stated	Gnansounou,2015
FR,	SHF	Enzymatic	S. cerevisiae	25 FPU/g	83	15.5	Moncada et al.,
indirect		saccharification					2016

Note: Yield as percentage of theoretical; FR-furfural residue; GS-Gledistsia saponin; SB-sugarcane bagasse

			Furfural pro	duction	action Ethanol production							
Biomass	Pretreatment	Method	Catalyst	T(∘C)	Furfural yield %	Microbial strain	fermentation	Ethanol Yield	Ethanol (g/L)	Refere	ence	;
Sugarcane bagasse	0.25%v/v H <sub>2</sub> SO <sub>4</sub> (120- 140°C), 90 to 180 min	Indirect	30% w/w Indion 130	170	59	Kluyveromyc	es sp. IIPE453	88%	17.1	Ghosh 2015	et	al.,
Sugarcane bagasse	Direct furfural production	Direct	0-1.25 %w/w H <sub>2</sub> SO4	175	53	S. cerevisiae	no.1701	87%	Not given	Mesa 2014	et	al.,
Corn stover	Direct furfural production	Direct	6% H <sub>3</sub> PO <sub>4</sub>	200	61	S. cerevisiae	NRRL- Y2034	92-99%	42.0	Avci 2013	et	al.,
Corn stover	0.03 wt% HCl + 5% ZnCl₂, 150 °C for 10 min then 170 °C	Indirect	0.03% HCl, 5% acidified ZnCl <sub>2</sub>	150	91	S. cerevisiae	ATCC 200062	69-98%	17.0	Yoo 2012	et	al.,
Dried oil palm Empty fruit bunch	1.025%v/v H₂SO₄ at 160 ℃	Indirect	No additional catalyst	198	91	S. cerevisiae	BY4741	61%	Not given	Ramai Gnans 2015	า oun	and ou,
Pinus patula bark (wood residue)	1% v/v NaOH at 121°C for 1 hr	Indirect	8% H <sub>2</sub> SO <sub>4</sub>	170	91	S. cerevisiae		83%	15.5	Monca al., 20	da 16	et

Table 2. 4: Summary of furfural and ethanol co-production experimental studies.

NB: Yield of furfural yield as percentage of the theoretical yield, the yield of ethanol is expressed as % of ethanol theoretical yield.



Figure 2. 1: Furfural and ethanol co-production in a biorefinery, a) one-stage furfural production integrated with simultaneous saccharification and fermentation (SSF) (Mesa et al., 2014), b) two-stage furfural production integrated with SSF (Moncada et al., 2016; Farzad et al., 2017)

	Faad	Ef	Eth an al			Total		<b>E</b> th an al	E		
Biomass	reea (t/h)	furfurai (t/h)	Ethanol (t/h)	Electricity (MW)	MPV (M.USD/y)	sales (M. USD/y)	IRR	(USD/L)	(USD/t)	(USD/kWh)	Reference
Pinus patula											Moncada et
bark	40	4.08	6.49	18.25	184.54	126.89	N.D	1.06	1200	0.1	al., 2016
											Farzad et
SB and HR	65	2.07	5.66	7.5	N.D	54.1	7.5	0.596	1200	0.08	al., 2017
								Not			Zhao and
Wheat Straw	25	2.83	4.09	6.62	N.D	N.D	N.D	stated	1500	0.12	Liu, 2019
				No						No	Hossain et
Corn stover	78	0.94	20.79	electricity	N.D	167.66	N.D	0.692	1700	electricity	al., 2019

Table 2. 5: Summary of process economics of ethanol and furfural co-production from lignocellulosic biomass.

\*N.D: Not determined by the authors of the paper. M.USD/y: Million United State Dollars per year. IRR: Internal rate of return. Purity of the furfural reported is at least 98 wt% and ethanol is 99.7 wt%. SB: sugarcane bagasse; HR: harvest residues,

## 2.7 Conclusions

Sequential co-production of furfural and ethanol in a biorefinery is a promising pathways for commercialisation of second generation ethanol, since the high value of furfural is hypothesised to result in attractive overall process economics. This literature review revealed the following three main gaps relating to the development of furfural and ethanol co-production process flowsheet as well as techno-economic evaluation of furfural and ethanol co-production biorefineries: -

## 2.7.1 Furfural production and corresponding ethanol yield from residual biomass

Studies focussed on the one-stage furfural process and ethanol co-production usually employ detoxification of furfural residues prior to ethanol production and generally do not provide ethanol yield data from furfural residues produced at various conditions. The relationship between furfural production conditions, the properties of the resulting solids and their enzymatic digestibility, and the impacts of these on subsequent ethanol production in a biorefinery has not been clearly outlined. Moreover, studies focussed on the one-stage furfural and ethanol co-production biorefineries have primarily employed the SHF fermentation technique. In the one-stage furfural and ethanol co-production system, ethanol production is affected by furfural production methods and conditions since cellulosic ethanol is sensitive to the properties of the solid residues after furfural production. In the two stagefurfural and ethanol process, ethanol and furfural yields are both affected by pretreatment conditions. Therefore, furfural and ethanol co-production has various combinations of production yields corresponding to various process economics. Considering the dependence of ethanol production on furfural production and conditions, the optimal conditions for co-

production may not necessarily correspond to the maximum yields of either product but yields below the attainable maximum.

## 2.7.2 Economics of the one-stage furfural process and ethanol co-production by SSF

Techno-economic assessment studies of the one-stage furfural process and ethanol co-produced from furfural residues obtained at different process conditions in a sequential biorefinery configuration are scarce in literature. The focus on techno-economic studies pertaining to furfural and ethanol co-production have primarily been on the two-stage furfural process followed by ethanol production using the SHF technique. The potential of the one-stage furfural process and ethanol co-production from furfural residues should not be neglected as the one-stage furfural process already operates at industrial scale and can potentially provide feedstock for cellulosic ethanol production at commercial scale. One major drawback of the one-stage furfural process is high energy consumption; however, furfural reactor configurations and use of low cost catalyst can reduce overall energy consumption. Improved overall energy demand of the one-stage furfural process can allow an energy self-sufficient one-stage and ethanol co-production biorefinery thereby preventing the use of fossil derived energy.

# 2.7.3 Techno-economic aspects of one-stage furfural and ethanol co-production versus two-stage furfural and ethanol co-production

Studies that compare techno-economics of the one-stage furfural and ethanol sequential production with biorefinery focussed on the two-stage furfural and ethanol co-production are

also scarce in literature. Similar to the one-stage furfural process, the two-stage furfural and ethanol co-production biorefinery economic studies have focussed on a single set of conditions, where only energy integration is conducted to improve the economics without considering the process economics at other process conditions. Most of the available technoeconomic studies focussed on the two-stage furfural process with ethanol co-production employ organic solvents for furfural purification and recovery, which cause environmental burdens. Moreover, the available techno-economic studies on the two-stage furfural process and ethanol co-production involve a detoxification of pretreated biomass and generally employ separate hydrolysis and fermentation technique.

## References

- Aguilar, R., Ramírez, J.A., Garrote, G., Vázquez, M., 2002. Kinetic study of the acid hydrolysis of sugar cane bagasse. J. Food Eng. 55, 309–318. https://doi.org/10.1016/S0260-8774(02)00106-1
- Albers, E., Larsson, C., Liden, G., Niklasson, C., Gustafsson, L., 1996. Influence of the Nitrogen Source on Saccharomyces cerevisiae Anaerobic Growth and Product Formation. Appl. Environ. Microbiol. 62, 3187–3195.
- Avci, A., Saha, B.C., Kennedy, G.J., Cotta, M.A., 2013. High temperature dilute phosphoric acid pretreatment of corn stover for furfural and ethanol production. Ind. Crops Prod. 50, 478–484. https://doi.org/10.1016/j.indcrop.2013.07.055
- Bamufleh, H.S., Alhamed, Y.A., Daous, M.A., 2013. Furfural from midribs of date-palm trees by sulfuric acid hydrolysis. Ind. Crop. Prod. 42, 421–428.

https://doi.org/10.1016/j.indcrop.2012.06.008

- Biddy, M.J., Scarlata, C., Christopher, K., 2016. Chemicals from Biomass: A Market Assessment of Bioproducts with Near-Term Potential, National Renewable Energy Laboratory.
- Bohre, A., Dutta, S., Saha, B., Abu-omar, M.M., 2015. Upgrading Furfurals to Drop-in
  Biofuels: An Overview. ACS Sustain. Chem. Eng. 3, 1263–1277.
  https://doi.org/10.1021/acssuschemeng.5b00271
- Boshoff, S., Gottumukkala, L.D., Rensburg, E. Van, Görgens, J., 2016. Paper sludge (PS) to bioethanol: Evaluation of virgin and recycle mill sludge for low enzyme , high-solids fermentation. Bioresour. Technol. 203, 103–111. https://doi.org/10.1016/j.biortech.2015.12.028
- Brienzo, M., Fikizolo, S., Benjamin, Y., Tyhoda, L., 2017. Influence of pretreatment severity on structural changes, lignin content and enzymatic hydrolysis of sugarcane bagasse samples. Renew. Energy 104, 271–280. https://doi.org/10.1016/j.renene.2016.12.037
- Bruce, S.M., Zong, Z., Chatzidimitriou, A., Avci, L.E., Bond, J.Q., Carreon, M.A., Wettstein,
  S.G., 2016. Small pore zeolite catalysts for furfural synthesis from xylose and
  switchgrass in a Y-valerolactone/water solvent. J. Mol. Catal. A Chem. 422, 18–22.
  https://doi.org/10.1016/j.molcata.2016.02.025
- Bu, L., Tang, Y., Xing, Y., Zhang, W., Shang, X., Jiang, J., 2014. Comparison of hydrophilic variation and bioethanol production of furfural residues after delignification pretreatment. Biosci. Biotechnol. Biochem. 78, 1435–1443.
   https://doi.org/10.1080/09168451.2014.921556

- Cai, C.M., Zhang, T., Kumar, R., Wyman, C.E., 2014. Integrated furfural production as a renewable fuel and chemical platform from lignocellulosic biomass. J. Chem. Technol. Biotechnol. 89, 2–10. https://doi.org/10.1002/jctb.4168
- Cardona, C.A., Quintero, J.A., Paz, I.C., 2010. Production of bioethanol from sugarcane bagasse: Status and perspectives. Bioresour. Technol. 101, 4754–4766. https://doi.org/10.1016/j.biortech.2009.10.097
- Chen, H., Qin, L., Yu, B., 2015. Furfural production from steam explosion liquor of rice straw by solid acid catalysts (HZSM-5). Biomass and Bioenergy 73, 77–83. https://doi.org/10.1016/j.biombioe.2014.12.013
- Clauser, N.M., Gutiérrez, S., Area, M.C., Felissia, F.E., Vallejos, M.E., 2016. Small-sized biorefineries as strategy to add value to sugarcane bagasse. Chem. Eng. Res. Des. 107, 137–146. https://doi.org/10.1016/j.cherd.2015.10.050
- Dalvand, K., Rubin, J., Gunukula, S., Wheeler, M.C., Hunt, G., 2018. Economics of biofuels : Market potential of furfural and its derivatives. Biomass and Bioenergy 115, 56–63. https://doi.org/10.1016/j.biombioe.2018.04.005
- Danon, B., Marcotullio, G., De Jong, W., 2013. Mechanistic and kinetic aspects of pentose dehydration towards furfural in aqueous media employing homogeneous catalysis. Green Chem. 1–16. https://doi.org/10.1039/b000000x
- Dashtban, M., Technologies, A., Dashtban, M., 2012. PRODUCTION OF FURFURAL: OVERVIEW AND CHALLENGES. J. Sci. Technol. For. Prod. Process. 2, 44–53.
- de Jong, W., Marcotullio, G., 2010. Overview of Biorefineries based on Co-Production of Furfural, Existing Concepts and Novel Developments. Int. J. Chem. React. Eng. 8, 1–24.

https://doi.org/10.2202/1542-6580.2174

- Deng, A., Lin, Q., Yan, Y., Li, H., Ren, J., Liu, C., Sun, R., 2016. A feasible process for furfural production from the pre-hydrolysis liquor of corncob via biochar catalysts in a new biphasic system. Bioresour. Technol. 216, 754–760. https://doi.org/10.1016/j.biortech.2016.06.002
- Du, J., Gao, H., Guan, J., Yu, G., Zhang, Y., Mu, X., 2015. Furfural Formation from Corn Cobs in a One-Pot Method Catalyzed by 808–812.
- Dussan, K., Girisuta, B., Haverty, D., Leahy, J.J., Hayes, M.H.B., 2013. Kinetics of levulinic acid and furfural production from Miscanthus×giganteus. Bioresour. Technol. 149, 216–224. https://doi.org/10.1016/j.biortech.2013.09.006
- Farzad, S., Mandegari, M.A., Guo, M., Haigh, K., Shah, N., Görgens, J.F., 2017. Multi-product biorefineries from lignocelluloses: A pathway to revitalisation of the Sugar Industry?
  Biotechnol. Biofuels 10, 1–24. https://doi.org/10.1186/s13068-017-0761-9
- Favaro, L., Viktor, M.J., Rose, S.H., Viljoen-Bloom, M., van Zyl, W.H., Basaglia, M., Cagnin, L.,
   Casella, S., 2015. Consolidated bioprocessing of starchy substrates into ethanol by
   industrial Saccharomyces cerevisiae strains secreting fungal amylases. Biotechnol.
   Bioeng. 112, 1751–1760. https://doi.org/10.1002/bit.25591
- García-Domínguez, M.T., García-Domínguez, J.C., Feria, M.J., Gómez-Lozano, D.M., López, F., Díaz, M.J., 2013. Furfural production from Eucalyptus globulus: Optimizing by using neural fuzzy models. Chem. Eng. J. 221, 185–192. https://doi.org/10.1016/j.cej.2013.01.099

Gebreyohannes, S., Neely, B.J., Gasem, K.A.M., 2014. One-parameter modified nonrandom

two-liquid (NRTL) activity coefficient model. Fluid Phase Equilib. 379, 196–205. https://doi.org/10.1016/j.fluid.2014.07.027

- Geddes, C.C., Mullinnix, M.T., Nieves, I.U., Hoffman, R.W., Sagues, W.J., York, S.W., Shanmugam, K.T., Erickson, J.E., Vermerris, W.E., Ingram, L.O., 2013. Seed train development for the fermentation of bagasse from sweet sorghum and sugarcane using a simplified fermentation process. Bioresour. Technol. 128, 716–724. https://doi.org/10.1016/j.biortech.2012.09.121
- Ghosh, D., Dasgupta, D., Agrawal, D., Kaul, S., Adhikari, D.K., Kurmi, A.K., Arya, P.K., Bangwal, D., Negi, M.S., 2015. Fuels and chemicals from lignocellulosic biomass: An integrated biorefinery approach. Energy and Fuels 29, 3149–3157.
  https://doi.org/10.1021/acs.energyfuels.5b00144
- Giuliano, A., Barletta, D., Poletto, M., 2018. Techno-economic assessment of a lignocellulosic biorefinery co-producing ethanol and xylitol or furfural. https://doi.org/10.1016/B978-0-444-64235-6.50105-4
- Gubicza, K., Nieves, I.U., Sagues, W.J., Barta, Z., Shanmugam, K.T., Ingram, L.O., 2016.
  Techno-economic analysis of ethanol production from sugarcane bagasse using a
  Liquefaction plus Simultaneous Saccharification and co-Fermentation process.
  Bioresour. Technol. 208, 42–48. https://doi.org/10.1016/j.biortech.2016.01.093
- Guo, Z., Olsson, L., 2016. Physiological responses to acid stress by Saccharomyces cerevisiae when applying high initial cell density. 2 FEMS Yeast Res. 16, 1–11. https://doi.org/10.1093/femsyr/fow072

Hanly, T.J., Henson, M.A., 2014. Dynamic Model-Based Analysis of Furfural and HMF

Detoxification by Pure and Mixed Batch Cultures of S . cerevisiae and S . stipitis. Biotechnol. Bioeng. 111, 272–284. https://doi.org/10.1002/bit.25101

- He, J., Zhang, W., Liu, X., Xu, N., Xiong, P., 2016. Optimization of prehydrolysis time and substrate feeding to improve ethanol production by simultaneous saccharification and fermentation of furfural process residue. J. Biosci. Bioeng. 122, 563–569. https://doi.org/10.1016/j.jbiosc.2016.04.012
- Hernández, V., Romero-garcía, J.M., Dávila, J.A., Castro, E., Cardona, C.A., 2014. Technoeconomic and environmental assessment of an olive stone based biorefinery. Resour. Conserv. Recycl. 92, 145–150. https://doi.org/10.1016/j.resconrec.2014.09.008
- Himmel, M.E., Ruth, M.F., Wyman, C.E., 1999. Cellulase for commodity products from cellulosic biomass. Curr. Opin. Biotechnol. 10, 358–364. https://doi.org/10.1016/S0958-1669(99)80065-2
- Hossain, S., Theodoropoulos, C., Yousuf, A., 2019. Techno-economic evaluation of heat integrated second generation bioethanol and furfural coproduction. Biochem. Eng. J. 144, 89–103. https://doi.org/10.1016/j.bej.2019.01.017
- Hu, F., Jung, S., Ragauskas, A., 2012. Pseudo-lignin formation and its impact on enzymatic hydrolysis. Bioresour. Technol. 117, 7–12.
   https://doi.org/10.1016/j.biortech.2012.04.037
- Humbird, D., Davis, R., Tao, L., Kinchin, C., Hsu, D., Aden, A., 2011. Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol: Dilute-Acid Pretreatment and Enzymatic Hydrolysis of Corn Stover, National Renewable Energy Laboratory.

- Jeon, Y.J., Xun, Z., Rogers, P.L., 2010. Comparative evaluations of cellulosic raw materials for second generation bioethanol production 518–524. https://doi.org/10.1111/j.1472-765X.2010.02923.x
- Ji, H., Chen, L., Zhu, J.Y., Gleisner, R., Zhang, X., 2016. Reaction Kinetics Based Optimization of Furfural Production from Corncob Using a Fully Recyclable Solid Acid. Ind. Eng. Chem. Res. 55, 11253–11259. https://doi.org/10.1021/acs.iecr.6b03243
- Ji, L., Zheng, T., Zhao, P., Zhang, W., Jiang, J., 2016. Ethanol production from a biomass mixture of furfural residues with green liquor-peroxide saccarified cassava liquid. BMC Biotechnol. 16, 1–11. https://doi.org/10.1186/s12896-016-0278-5
- Jin, E., Mendis, G.P., Sutherland, J.W., 2019. Integrated sustainability assessment for a bioenergy system: A system dynamics model of switchgrass for cellulosic ethanol production in the U. S. midwest. J. Clean. Prod. 234, 503–520. https://doi.org/10.1016/j.jclepro.2019.06.205
- Kapanji, K.K., Haigh, K.F., Görgens, J.F., 2019. Techno-economic analysis of chemically catalysed lignocellulose biorefineries at a typical sugar mill : Sorbitol or glucaric acid and electricity. Bioresour. Technol. 289, 121635.
  https://doi.org/10.1016/j.biortech.2019.121635
- Katsimpouras, C., Kalogiannis, K.G., Kalogianni, A., Lappas, A.A., 2017. Production of high concentrated cellulosic ethanol by acetone / water oxidized pretreated beech wood. Biotechnol. Biofuels 10, 1–16. https://doi.org/10.1186/s13068-017-0737-9
- Kazi, F.K., Patel, A.D., Serrano-ruiz, J.C., Dumesic, J.A., Anex, R.P., 2011. Techno-economic analysis of dimethylfuran (DMF) and hydroxymethylfurfural (HMF) production from

pure fructose in catalytic processes. Chem. Eng. J. 169, 329–338. https://doi.org/10.1016/j.cej.2011.03.018

- Lavarack, B.P., Griffin, G.J., Rodman, D., 2002. The acid hydrolysis of sugarcane bagasse hemicellulose to produce xylose,arabinose,glucose and other products. Biomass and Bioenergy 23, 367–380.
- Li, H., Wang, X., Liu, C., Ren, J., Zhao, X., Sun, R., Wu, A., 2016. An efficient pretreatment for the selectively hydrothermal conversion of corncob into furfural: The combined mixed ball milling and ultrasonic pretreatments. Ind. Crops Prod. 94, 721–728. https://doi.org/10.1016/j.indcrop.2016.09.052
- Lin, Q., Li, H., Ren, J., Deng, A., Li, W., Liu, C., Sun, R., 2017. Production of xylooligosaccharides by microwave-induced, organic acid-catalyzed hydrolysis of different xylan-type hemicelluloses: Optimization by response surface methodology. Carbohydr. Polym. 157, 214–225. https://doi.org/10.1016/j.carbpol.2016.09.091
- Liu, L., Chang, H. min, Jameel, H., Park, S., 2018. Furfural production from biomass
  pretreatment hydrolysate using vapor-releasing reactor system. Bioresour. Technol.
  252, 165–171. https://doi.org/10.1016/j.biortech.2018.01.006
- Mandegari, M.A., Farzad, S., Görgens, J.F., 2017a. Economic and environmental assessment of cellulosic ethanol production scenarios annexed to a typical sugar mill. Bioresour. Technol. 224, 314–326. https://doi.org/10.1016/j.biortech.2016.10.074
- Mandegari, M.A., Farzad, S., van Rensburg, E., Görgens, J.F., 2017b. Multi-criteria analysis of a biorefi nery for co-production of lactic acid and ethanol from sugarcane lignocellulose. Biofuels, Bioprod. Biorefining 11, 971–990. https://doi.org/10.1002/bbb

- Mao, L., Zhang, L., Gao, N., Li, A., 2012. FeCl 3 and acetic acid co-catalyzed hydrolysis of corncob for improving furfural production and lignin removal from residue. Bioresour.
   Technol. 123, 324–331. https://doi.org/10.1016/j.biortech.2012.07.058
- Mesa, L., Martínez, Y., Barrio, E., González, E., 2017. Desirability function for optimization of
   Dilute Acid pretreatment of sugarcane straw for ethanol production and preliminary
   economic analysis based in three fermentation configurations. Appl. Energy 198, 299–
   311. https://doi.org/10.1016/j.apenergy.2017.03.018
- Mesa, L., Morales, M., González, E., Cara, C., Romero, I., Castro, E., Mussatto, S.I., 2014.
  Restructuring the processes for furfural and xylose production from sugarcane bagasse
  in a biorefinery concept for ethanol production. Chem. Eng. Process. Process Intensif.
  85, 196–202. https://doi.org/10.1016/j.cep.2014.07.012
- Metkar, P.S., Till, E.J., Corbin, D.R., Pereira, C.J., Hutchenson, K.W., Sengupta, S.K., 2015. furfural using solid acid catalysts †. Green Chem. 17, 1453–1466. https://doi.org/10.1039/c4gc01912a
- Mohlala, L.M., Bodunrin, M.O., Awosusi, A.A., Daramola, M.O., Cele, N.P., Olubambi, P.A.,
  2016. Beneficiation of corncob and sugarcane bagasse for energy generation and
  materials development in Nigeria and South Africa: A short overview. Alexandria Eng. J.
  55, 3025–3036. https://doi.org/10.1016/j.aej.2016.05.014
- Mokomele, T., Sousa, C., Balan, V., Rensburg, E. Van, Dale, B.E., Görgens, J.F., 2018. Ethanol production potential from AFEX <sup>™</sup> and steam - exploded sugarcane residues for sugarcane biorefineries. Biotechnol. Biofuels 11, 1–21. https://doi.org/10.1186/s13068-018-1130-z
- Moncada, J., Cardona, C.A., Higuita, J.C., Vélez, J.J., López-Suarez, F.E., 2016. Wood residue (Pinus patula bark) as an alternative feedstock for producing ethanol and furfural in Colombia: Experimental, techno-economic and environmental assessments. Chem. Eng. Sci. 140, 309–318. https://doi.org/10.1016/j.ces.2015.10.027
- Neves, P. V, Pitarelo, A.P., Ramos, L.P., 2016. Production of cellulosic ethanol from sugarcane bagasse by steam explosion: Effect of extractives content, acid catalysis and different fermentation technologies. Bioresour. Technol. 208, 184–194. https://doi.org/10.1016/j.biortech.2016.02.085
- Nguyen, T.Y., Cai, C.M., Osman, O., Kumar, R., Wyman, C.E., 2016. CELF pretreatment of corn stover boosts ethanol titers and yields from high solids SSF with low enzyme loadings. Green Chem. 1581–1589. https://doi.org/10.1039/c5gc01977j
- Nhien, L.C., Long, N.V.D., Kim, S., Lee, M., 2016. Design and optimization of intensified
   biorefinery process for furfural production through a systematic procedure. Biochem.
   Eng. J. 116, 166–175. https://doi.org/10.1016/j.bej.2016.04.002
- Nieder-Heitmann, M., Haigh, K.F., Görgens, J.F., 2018. Process design and economic analysis of a biore fi nery co-producing itaconic acid and electricity from sugarcane bagasse and trash lignocelluloses. Bioresour. Technol. 262, 159–168. https://doi.org/10.1016/j.biortech.2018.04.075
- Özüdoğru, H.M.R., Haigh, K.F., Görgens, J.F., 2019. Techno-economic analysis of product biorefineries utilizing sugarcane lignocelluloses : Xylitol , citric acid and glutamic acid scenarios annexed to sugar mills with electricity co-production. Ind. Crop. Prod. 133, 259–268. https://doi.org/10.1016/j.indcrop.2019.03.015

- Pabari, R.M., Ramtoola, Z., 2012. Application of face centred central composite design to optimise compression force and tablet diameter for the formulation of mechanically strong and fast disintegrating orodispersible tablets. Int. J. Pharm. 430, 18–25. https://doi.org/10.1016/j.ijpharm.2012.03.021
- Panahi, H.S.K., Dehhaghi, M., Kinder, J.E., Ezeji, T.C., 2019. A review on green liquid fuels for the transportation sector : a prospect of microbial solutions to climate change. Biofuel Res. J. 23, 995–1024. https://doi.org/10.18331/BRJ2019.6.3.2
- Patel, H., Chapla, D., Shah, A., 2017. Bioconversion of pretreated sugarcane bagasse using enzymatic and acid followed by enzymatic hydrolysis approaches for bioethanol production. Renew. Energy 109, 323–331.

https://doi.org/10.1016/j.renene.2017.03.057

- Petersen, A.M., Haigh, K., Görgens, J.F., 2014. Techno-economics of integrating bioethanol production from spent sulfite liquor for reduction of greenhouse gas emissions from sulfite pulping mills. Biotechnol. Biofuels 7, 1–14. https://doi.org/10.1186/s13068-014-0169-8
- Prajapati, B.P., Jana, U.K., Suryawanshi, R.K., Kango, N., 2020. Sugarcane bagasse sacchari fi cation using Aspergillus tubingensis enzymatic cocktail for 2G bio-ethanol production. Renew. Energy 152, 653–663. https://doi.org/10.1016/j.renene.2020.01.063
- Qing, Q., Guo, Q., Zhou, L., Wan, Y., Xu, Y., Ji, H., Gao, X., Zhang, Y., 2017. Catalytic conversion of corncob and corncob pretreatment hydrolysate to furfural in a biphasic system with addition of sodium chloride. Bioresour. Technol. 226, 247–254. https://doi.org/10.1016/j.biortech.2016.11.118

Raman, J.K., Gnansounou, E., 2015. Furfural production from empty fruit bunch - A biorefinery approach. Ind. Crops Prod. 69, 371–377.
https://doi.org/10.1016/j.indcrop.2015.02.063

Rocha, G.J.M., Martin, C., da Silva, V.F.N., Gomez, E.O., Goncalves, A.R., 2012. Mass balance of pilot-scale pretreatment of sugarcane bagasse by steam explosion followed by alkaline delignification. Bioresour. Technol. 111, 447–452.
https://doi.org/10.1016/j.biortech.2012.02.005

- Rosales-Calderon, O., Arantes, V., 2019. A review on commercial- scale high-value products that can be produced alongside cellulosic ethanol. Biotechnol. Biofuels 12, 1–58. https://doi.org/10.1186/s13068-019-1529-1
- Sánchez, C., Serrano, L., Andres, M.A., Labidi, J., 2013. Furfural production from corn cobs autohydrolysis liquors by microwave technology. Ind. Crops Prod. 42, 513–519. https://doi.org/10.1016/j.indcrop.2012.06.042
- Schmidt, L.M., Mthembu, L.D., Reddy, P., Deenadayalu, N., Kaltschmitt, M., Smirnova, I., 2017. Levulinic acid production integrated into a sugarcane bagasse based biorefinery using thermal-enzymatic pretreatment. Ind. Crops Prod. 99, 172–178. https://doi.org/10.1016/j.indcrop.2017.02.010
- Shi, X., Zhao, B., Zhou, H., Tian, Y., Qiao, Y., Ji, B., 2019. Direct Saccharification and
  Fermentation for High Glucose and Ethanol Production from Non-Detoxified Furfural
  Residue Without Any Pretreatment. Energy Technol. Environ. Sci. 4, 7844–7850.
  https://doi.org/10.1002/slct.201901367

Shinde, S.D., Meng, X., Kumar, R., Ragauskas, A.J., 2018. Recent advances in understanding

the pseudo-lignin formation in a lignocellulosic biorefinery. Green Chem. 20, 2192– 2205. https://doi.org/10.1039/c8gc00353j

- Silva, J.F.L., Selicani, M.A., Junqueira, T.L., Klein, B.C., Vaz, S., Bonomi, A., 2017. Integrated furfural and first generation bioethanol production: Process simulation and technoeconomic analysis. Brazilian J. Chem. Eng. 34, 623–634. https://doi.org/10.1590/0104-6632.20170343s20150643
- Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., Crocker, D., 2012. Determination of Structural Carbohydrates and Lignin in Biomass, National Renewable Energy Laboratory, Technical Report NREL/TP-510-42618, Revised August 2012.

Smithers, J., 2014. Review of sugarcane trash recovery systems for energy cogeneration in South Africa. Renew. Sustain. Energy Rev. 32, 915–925.

https://doi.org/10.1016/j.rser.2014.01.042

- Steinbach, D., Kruse, A., Sauer, J., 2017. Pretreatment technologies of lignocellulosic
   biomass in water in view of furfural and 5-hydroxymethylfurfural production- A review.
   Biomass Convers. Biorefinery. https://doi.org/10.1007/s13399-017-0243-0
- Sun, S.N., Cao, X.F., Li, M.F., Xu, F., Sun, R.C., 2013. Treatment of Furfural Residue by Solvent Extraction for Enzymatic Hydrolysis: Effect of Delignification on the Structure and Digestibility. Bioenergy Res. 6, 1022–1029. https://doi.org/10.1007/s12155-013-9329-0
- Tabatabaei, M., Mortaza, A., Valijanian, E., Panahi, H.K.S., Nizami, A.-S., Ghanavati, H., Sulaiman, A., Mirmohamadsadeghi, S., Karimi, K., 2020. A comprehensive review on recent biological innovations to improve biogas production, Part 1 : Upstream strategies. Renew. Energy 146, 1204–1220.

https://doi.org/https://doi.org/10.1016/j.renene.2019.07.037

- Unrean, P., Ketsub, N., 2018. Integrated lignocellulosic bioprocess for co-production of ethanol and xylitol from sugarcane bagasse. Ind. Crop. Prod. 123, 238–246.
- Unrean, P., Khajeeram, S., 2016. Optimization and techno-economic assessment of highsolid fed-batch sacchari fi cation and ethanol fermentation by Scheffersomyces stipitis and Saccharomyces cerevisiae consortium. Renew. Energy 99, 1062–1072. https://doi.org/10.1016/j.renene.2016.08.019
- Unrean, P., Khajeeram, S., Laoteng, K., 2016. Systematic optimization of fed-batch simultaneous saccharification and fermentation at high-solid loading based on enzymatic hydrolysis and dynamic metabolic modeling of Saccharomyces cerevisiae.
  Appl. Microbiol. Biotechnol. 100, 2459–2470. https://doi.org/10.1007/s00253-015-7173-1
- Uppal, S.K., Kaur, R., 2011. Hemicellulosic Furfural Production from Sugarcane Bagasse Using Different Acids. Sugar Tech 13, 166–169. https://doi.org/10.1007/s12355-011-0081-5
- Vallejos, M.E., Felissia, F.E., Kruyeniski, J., Area, M.C., 2015. Kinetic study of the extraction of hemicellulosic carbohydrates from sugarcane bagasse by hot water treatment. Ind. Crops Prod. 67, 1–6. https://doi.org/10.1016/j.indcrop.2014.12.058
- Vázquez, M., Oliva, M., Téllez-Luis, S.J., Ramírez, J.A., 2007. Hydrolysis of sorghum straw using phosphoric acid: Evaluation of furfural production. Bioresour. Technol. 98, 3053– 3060. https://doi.org/10.1016/j.biortech.2006.10.017
- Wang, K., Yang, H., Chen, Q., Sun, R. cang, 2013. Influence of delignification efficiency with alkaline peroxide on the digestibility of furfural residues for bioethanol production.

Bioresour. Technol. 146, 208–214. https://doi.org/10.1016/j.biortech.2013.07.008

- Wang, W., Ren, J., Li, H., Deng, A., Sun, R., 2015. Direct transformation of xylan-type hemicelluloses to furfural via SnCl4 catalysts in aqueous and biphasic systems.
  Bioresour. Technol. 183, 188–194. https://doi.org/10.1016/j.biortech.2015.02.068
- Wang, X., Fai, Y., Li, Y., Ma, X., Cui, S., Zhang, T., 2017. Inhibitory e ff ects of phenolic compounds of rice straw formed by sacchari fi cation during ethanol fermentation by Pichia stipitis. Bioresour. Technol. 244, 1059–1067.
  https://doi.org/10.1016/j.biortech.2017.08.096
- Wang, Z., Zhuge, J., Fang, H., Prior, B.A., 2001. Glycerol production by microbial fermentation : A review. Biotechnol. Adv. 19 19, 201–223.
- Watanabe, K., Tachibana, S., Konishi, M., 2019. Modeling growth and fermentation inhibition during bioethanol production using component pro fi les obtained by performing comprehensive targeted and non-targeted analyses. Bioresour. Technol. 281, 260–268. https://doi.org/10.1016/j.biortech.2019.02.081
- Xing, R., Wei, Q., Huber, G.W., 2011. Production of furfural and carboxylic acids from waste aqueous hemicellulose solutions from the pulp and paper and cellulosic ethanol industries<sup>†</sup>. Energy Environ. Sci. 4, 2193–2205. https://doi.org/10.1039/c1ee01022k
- Xing, Y., Bu, L., Sun, D., Liu, Z., Liu, S., Jiang, J., 2016. Enhancement of high-solids enzymatic hydrolysis and fermentation of furfural residues by addition of Gleditsia saponin. FUEL 177, 142–147. https://doi.org/10.1016/j.fuel.2016.03.024
- Xu, K., Seo, Y., Li, J., Li, C., 2019. Resistance mechanisms and reprogramming of microorganisms for e ffi cient biore fi nery under multiple environmental stresses.

Synth. Syst. Biotechnol. J. 4, 92–98. https://doi.org/10.1016/j.synbio.2019.02.003

- Xu, Y., Wang, D., 2017. Integrating starchy substrate into cellulosic ethanol production to boost ethanol titers and yields. Appl. Energy 195, 196–203. https://doi.org/10.1016/j.apenergy.2017.03.035
- Yan, K., Wu, G., Lafleur, T., Jarvis, C., 2014. Production, properties and catalytic
   hydrogenation of furfural to fuel additives and value-added chemicals. Renew. Sustain.
   Energy Rev. 38, 663–676. https://doi.org/10.1016/j.rser.2014.07.003
- Yemiş, O., Mazza, G., 2012. Optimization of furfural and 5-hydroxymethylfurfural production from wheat straw by a microwave-assisted process. Bioresour. Technol. 109, 215–223. https://doi.org/10.1016/j.biortech.2012.01.031
- Yemiş, O., Mazza, G., 2011. Acid-catalyzed conversion of xylose, xylan and straw into furfural by microwave-assisted reaction. Bioresour. Technol. 102, 7371–7378. https://doi.org/10.1016/j.biortech.2011.04.050
- Yoo, C.G., Kuo, M., Kim, T.H., 2012. Ethanol and furfural production from corn stover using a hybrid fractionation process with zinc chloride and simultaneous saccharification and fermentation (SSF). Process Biochem. 47, 319–326. https://doi.org/10.1016/j.procbio.2011.11.018
- Zabed, H., Sahu, J.N., Suely, A., Boyce, A.N., Faruq, G., 2017. Bioethanol production from renewable sources: Current perspectives and technological progress. Renew. Sustain.
   Energy Rev. 71, 475–501. https://doi.org/10.1016/j.rser.2016.12.076
- Zang, G., Shah, A., Wan, C., 2020. Techno-economic analysis of an integrated biore fi nery strategy based on one-pot biomass fractionation and furfural production. J. Clean.

Prod. 260, 120837. https://doi.org/10.1016/j.jclepro.2020.120837

- Zeitsch, K.J.J., 2000. The chemistry and technology of furfural and its many by-products, Sugar Series Vol. 13, Elsevier, The Netherlands. https://doi.org/10.1016/S1385-8947(00)00182-0
- Zhang, L., Xi, G., Zhang, J., Yu, H., Wang, X., 2017. Efficient catalytic system for the direct transformation of lignocellulosic biomass to furfural and 5-hydroxymethylfurfural. Bioresour. Technol. 224, 656–661. https://doi.org/10.1016/j.biortech.2016.11.097
- Zhang, X., Bai, Y., Cao, X., Sun, R., 2017. Pretreatment of Eucalyptus in biphasic system for furfural production and accelerated enzymatic hydrolysis. Bioresour. Technol. 238, 1–6. https://doi.org/10.1016/j.biortech.2017.04.011
- Zhao, M., Shi, D., Lu, X., Zong, H., Zhuge, B., Ji, H., 2019. Ethanol fermentation from nondetoxified lignocellulose hydrolysate by a multi-stress tolerant yeast Candida glycerinogenes mutant. Bioresour. Technol. 273, 634–640. https://doi.org/10.1016/j.biortech.2018.11.053
- Zhao, X., Liu, D., 2019. Multi-products co-production improves the economic feasibility of cellulosic ethanol : A case of Formiline pretreatment-based biore fi ning. Appl. Energy 250, 229–244.

#### **Chapter 3: Research aim and objectives**

In a biorefinery system that co-produces ethanol and furfural, the first stage of furfural/pretreatment process affects the properties of the solids residue used as feedstock for ethanol production. This occurs despite the fact that furfural and ethanol are produced from different components of the sugarcane bagasse. The one stage furfural process tends to favour furfural production, however, it is associated with cellulose degradation needed for ethanol production and produces yeast inhibitors. The pretreatment conditions in the two-stage furfural process determine amount of hemicellulosic sugars recovered for use as furfural feedstock and the digestibility of cellu-lignin solids used as ethanol feedstock. Therefore, there is a compromise in the yields of furfural and ethanol in a co-production biorefinery, which will have an effect on the economic outcome. This chapter details the aims and objectives of this study emanating from identified gaps in literature and highlights novel contributions.

# **3.1** Contribution 1: Experimental investigation into one-stage furfural production followed by ethanol production from furfural solid residues

#### 3.1.1 Statement of Novelty

The development of biorefineries for the one-stage furfural and ethanol coproduction requires furfural and ethanol yield data from unwashed furfural residues obtained in a sequential manner at various furfural process conditions. Current studies focused on ethanol production from furfural residues obtained using the one-stage furfural process generally provide a single set of furfural and ethanol yield data. Moreover, studies show that washing and delignification of the furfural residues produced by the one-stage furfural process prior to fermentation is required to remove yeast inhibitors and residual lignin as it interferes with enzymatic hydrolysis and yeast.

As part of this contribution, the study aims to evaluate the effects of the one-stage furfural production conditions on the yields of both furfural and ethanol production (from FR) when using the SSF technique without washing (detoxification) or delignification of FR prior to hydrolysis-fermentation. The study explores the relationship between furfural and ethanol yields, when one-stage furfural production from lignocellulose is combined with ethanol production from residual biomass using the SSF method, without washing of residues before SSF. The study also investigated digestibility, inhibitor concentration levels and fermentation (ethanol concentration) of industrial furfural residues to evaluate whether the available industrial yeast can be employed without any detoxification.

#### 3.1.2 Research objectives

The objectives associated with this contribution were:

- To investigate effects of one-stage furfural production conditions on furfural yield and ethanol from fermentation of unwashed residual biomass considering that the onestage furfural process affects the properties of the resulting cellu-lignin solids and their fermentation to ethanol.
- To investigate the effects of furfural production conditions on formation of organic acids which also act as yeast inhibitors when entrained in solids used as ethanol feedstock

• To determine the optimum feedstock conversion to furfural and ethanol in a sequential biorefinery set-up

The work conducted to fill the literature gap pertaining to lack of furfural yield and corresponding ethanol yield data from furfural residues produced at various conditions is detailed in Chapter 4.

# 3.2 Contribution 2: Process simulations and techno-economics of one-stage furfural production followed by ethanol production from furfural solid residues

#### 3.2.1 Statement of Novelty

Technical and economic aspects of ethanol produced alongside the one-stage furfural process in a biorefinery approach without detoxification of furfural residues and without the use of organic solvents for furfural separation are lacking in literature. In essence, there is a need for techno-economic data that can be used as a basis for selection of process configurations and conditions for cost effective co-production of ethanol and furfural from lignocellulosic biomass. This contribution aims to provide techno-economic analysis of the one-stage furfural and ethanol co-production at different furfural process conditions without any pretreatment prior to fermentation. Effects of the one-stage furfural production conditions and scale on minimum ethanol selling price were also included as part of this contribution.

#### 3.2.2 Research objectives

The objectives associated with this contribution 2 were:

- To investigate how furfural production conditions, and their impacts on subsequent ethanol production, affect process economics (minimum ethanol selling price(MESP))
- To evaluate how production scale affect minimum ethanol selling price as an indicator of profitability of a furfural-ethanol co-production biorefinery.
- To investigate how do the energy demands influence the process economics
- To determine whether producing from both hemicellulose and cellulose, in a similar annexed biorefinery, with the same amount of lignocelluloses available and the same sugar mill configuration, is economically less attractive based on IRR and MESP than the furfural-ethanol co-production scenario
- To investigate how sending furfural residues to the boiler or to ethanol production affect overall process economics by comparing furfural only biorefinery with integrated furfural and ethanol biorefinery

Chapter 5 entails the work conducted to fill the literature gap pertaining to lack of technoeconomic analysis of one-stage-furfural and ethanol co-production from furfural residues produced at various conditions.

### 3.3 Contribution 3: Techno-economic aspects of one-stage furfural and ethanol coproduction versus two-stage furfural and ethanol co-production

#### 3.3.1 Statement of Novelty

The economics of the two-stage furfural process has been previously studied, however, furfural separation was carried out using organic solvents. The use of organic solvents for furfural separation has been shown to increase energy demands since the organic solvents have to be recovered in order to reduce reagents costs and results in negative environmental impacts. Moreover, the available studies evaluate economic performance from one set of furfural and ethanol yield data, which neglects exploring economic potential of other conditions suitable for furfural and ethanol. Another important literature gap identified this contribution plans to fill is the lack of studies comparing the techno-economic aspects of the one-stage and two-stage furfural and ethanol co-production biorefineries using the same feedstock, in this case, sugarcane bagasse.

#### 3.3.2 Research objectives

The objectives associated with this contribution were:

- To determine how the process economics of the one-stage furfural and ethanol coproduction biorefinery compare to the process economics of the two-stage furfural and ethanol biorefinery that employs conventional furfural distillation configuration for recovery and purification of furfural.
- Investigate how production scale affects minimum ethanol selling price from twostage furfural and ethanol biorefinery
- To investigate how the energy demands influence the process economics of the twostage furfural and ethanol biorefinery

Chapter 6 entails the work conducted to fill the literature gap pertaining to lack of studies outlining techno-economic aspects of the one-stage furfural and ethanol co-production biorefinery in comparison to the process economics of the two-stage furfural and ethanol biorefinery.

#### Chapter 4: One-stage furfural and ethanol co-production

Chapter submitted in: This chapter was submitted to Biomass Conversion and Biorefinery Journal that has an Impact Factor of 2.602 (2019)
Title: Furfural production from sugarcane bagasse along with co-production of ethanol from furfural residues
Authors: Rhulani N. Ntimbani, Somayeh Farzad, Johann F. Görgens
Declaration: This chapter has been published in Biomass Conversion and Biorefinery Journal. It has been reproduced in this dissertation as is with the permission of Springer Nature

#### Objectives of this chapter in dissertation and findings

The research objectives highlighted in Contribution 1 are addressed in this chapter. One-stage furfural production experiments at various conditions (170-200°C, 0-2 wt.% H<sub>2</sub>SO<sub>4</sub>) followed by ethanol production experiments from each of the produced unwashed furfural solid residues were conducted to determine effects of furfural production on ethanol yields. The study also included fermentation of industrial furfural residues to evaluate whether the yeast strains employed could survive environment created by residual biomass obtained from industrial furfural reactor conditions.

The most favourable conditions for one-stage furfural and ethanol integrated biorefinery resulted in a compromise of both furfural and ethanol yield. Cellulose degradation, pseudo-lignin formation and yeast inhibitors negatively affect ethanol production from furfural residues obtained by the one-stage method. Furfural and ethanol yield data generated in this chapter was used to develop one-stage furfural and ethanol coproduction biorefinery scenarios, which were then subjected to techno-economic assessment (Chapter 5).

#### **Declaration by the candidate:**

With regards to Chapter 4, page numbers 74-105 of this dissertation, the nature and scope of my contributions were as follows:

Nature of contribution	Extent of contribution (%)
Experimental planning	95
Executing experiments	100
Interpretation of results	90
Writing the chapter	100

The following co-authors have contributed to Chapter 4 pages 74-105 in the dissertation in the following manner:

Name	E-mail address	Nature of contribution	Extent of contribution (%)		
		<ul> <li>Experimental</li> </ul>	5		
Somayeh Farzad		planning			
	<u>sfarzad@sun.ac.za</u>	<ul> <li>Interpretation of</li> </ul>	5		
		results			
		<ul> <li>Reviewing chapter</li> </ul>	40		
Johann Fordinand		<ul> <li>Interpretation of</li> </ul>	5		
Görgons	jgorgens@sun.ac.za	results			
OUISEIIS		<ul> <li>Reviewing chapter</li> </ul>	60		

Candidate signature:....

Date:....

Declaration with signature in possession of candidate and supervisor.

#### **Declaration by co-authors**

All authors read and approved this manuscript and hereby confirm that:

I. The declaration above accurately reflects the nature and extent of the contributions of the candidates and co-authors to Chapter 4, page numbers 74-105 in the dissertation,

II. No other authors contributed to Chapter 4, page numbers 74-105 in the dissertation beside those specified above, and

III. Potential conflicts of interest have been revealed to all interested parties and that are necessary arrangements have been made to use the material in Chapter 4 of the dissertation.

# Furfural production from sugarcane bagasse along with co-production of ethanol from furfural residues

Rhulani N. Ntimbani, Somayeh Farzad\*, Johann F. Görgens

Department of Process Engineering, Stellenbosch University, Private Bag X1, Stellenbosch

7602, South Africa

\*Corresponding author. Tel.: +27 21 808 9485; fax: +27 21 808 2059. E-mail address: sfarzad@sun.ac.za

#### Abstract

Cellulosic ethanol production from non-detoxified furfural residues produced at different operating conditions from sugarcane bagasse was investigated. Simultaneous saccharification and fermentation (SSF) technique and preconditioned industrial strains of *Saccharomyces cerevisiae*, i.e., EthanolRed<sup>®</sup> and CelluX<sup>™</sup>4 were used for fermentation. The highest furfural yield of 69% (11.44 g/100g of dry bagasse) was achieved at 170°C and 0.5 wt.% H<sub>2</sub>SO<sub>4</sub> (170-200°C and 0-1 wt.% H<sub>2</sub>SO<sub>4</sub>), with corresponding ethanol yields of 77-95% (9.57-11.58 g/100g of dry bagasse). The mass of ethanol produced reflected conversion of about 50% of cellulose in raw biomass due to cellulose degradation during furfural production. No production conditions could be found where both furfural and ethanol yields were maximised, indicating an unavoidable compromise between the two co-products. Furfural production conditions that provided an acceptable compromise between furfural and ethanol during co-production from sugarcane bagasse were 170°C and 0.25 wt.% H<sub>2</sub>SO<sub>4</sub>, resulting in furfural mass of 7.64g/100g of dry bagasse and ethanol mass of 9.86 and 10.91g/100g of dry bagasse when using EthanolRed<sup>®</sup> and CelluX<sup>™</sup>4, respectively.

Keywords: furfural, ethanol, fermentation, yeast inhibition, sugarcane bagasse, lignocellulose

#### 1 Introduction

Fossil-based fuels are regarded as major contributors to greenhouse gas emissions and the resulting adverse phenomena, i.e., global warming and climate change [1–4]. Among the alternatives available, furfural conversion to jet and diesel fuels has potential to partially replace petroleum-derived fuels and drive furfural market growth [5, 6]. Furfural is a platform chemical and majority of furfural is currently used to produce furfuryl alcohol [5, 7]. Other furfural applications are in the manufacturing of plastics, pharmaceuticals, agro-chemical products and non-petroleum-derived chemicals [8, 9].

In theory, any material containing a large amount of pentose (five carbon) sugars, such as arabinose and xylose, can serve as a raw material for furfural production [9–11]. However, furfural production is not economically viable without a low-cost feedstock [9]. Lignocellulosic material can be converted to furfural and a variety of biobased chemicals/fuels such as ethanol, butanol, xylose, glucose and levulinic acid [9, 12]. Conversion of lignocelluosic materials to value added products at high selectivity and yield at an economical cost that is comparable to fossil-derived products is challenging [13]. Since furfural is solely produced from the pentosans component of lignocellulose, co-production of cellulosic ethanol from cellulose-rich furfural residues (FR) has been proposed as a potential pathway to improve the value extracted from the lignocellulose feed of the furfural process [9, 14].

Furfural is generally produced using the one-stage process at industrial scale employing steam stripping in either batch or continuous operation directly from the lignocellulosic biomass feedstock [15–17]. One-stage furfural production by industrial processes is conducted at temperatures of 153-240°C with acid dosages up to 15 wt.% of dry feed, or under autocatalytic hydrolysis conditions in the same temperature range of 153-240°C from 40-120

minutes [9, 11]. These furfural process conditions are somewhat similar to those applied during lignocellulose pretreatment for ethanol production, e.g. dilute acid (0.1-6.0 wt.%  $H_2SO_4$  in solution) pretreatment at a temperatures of 121-220°C with residence time range of 1-300 minutes [18, 19].

Alternatively, furfural may also be produced from lignocelluloses in a two-stage process, where the hemicelluloses are first extracted from the lignocelluloses, followed by conversion of hemicellulose sugars to furfural in a separate processing unit [16, 20]. While the one-stage furfural production requires fewer process units, and is therefore associated with lower capital costs [21], the two-stage process offers the advantage of maximising the furfural and ethanol yields in separate process units, providing opportunity to reach higher yields in a co-production scenario [22]. However, due to more complex processing requirements (higher capital costs), the two-stage furfural production method is presently not applied for industrial furfural production [16, 20]. Since the one-stage furfural process is used industrially, utilisation of furfural residues as feedstock for ethanol production offers an opportunity for second generation ethanol production at commercial scale [11, 23].

The possibility of furfural and ethanol co-production has been investigated in previous studies, with focus mainly on fermentation of furfural residues obtained from industrial furfural residues produced at severe conditions [24, 25]. Harsh furfural production conditions promote pseudo-lignin formation which inhibits both enzymes and yeast, thus, washing and delignification of the FR is usually required prior to fermentation to render the solids more digestible [26, 27]. Washing and delignification of FR requires large amounts of water and reagents, which need to be treated downstream to meet environmental regulations [23, 24]. However, few studies show that detoxification alone is sufficient for fermentation of FR from

less severe furfural conditions process [11, 21]. Other detoxification steps include use of adsorbents and ultrafiltration, but these measures have similar drawbacks to washing and delignification. Alternatively, pressing of solids residues will decrease the concentrations of inhibitors, and process water requirements are thus also reduced [23, 28].

Furthermore, fermentation yeast strains with higher inhibitor tolerance have been genetically engineered to deal with yeast inhibition challenges as a preferred solution to detoxification of FR. The genetic and metabolic capabilities of engineered industrial yeast strains to tolerate certain levels of inhibitors are promoted when they are preconditioned by exposure of the inoculum to inhibitors similar to the fermentation media prior to fermentation [29, 30]. The probability of yeast cells survival in stressful environment is also increased by ensuring a higher initial biomass concentration [29–31].

Industrial fermentation yeasts can successfully convert sugars liberated from detoxified FR to ethanol using either separate hydrolysis and fermentation (SHF) or simultaneous saccharification and fermentation (SSF) [11, 21, 27]. Both enzymatic hydrolysis and fermentation occur in a single process unit when SSF is employed, which reduces associated capital expenses [32]. Another advantage offered by the SSF technique is less inhibition of cellulase by accumulation of sugars [32].

The relationship between furfural and ethanol produced when the one-stage furfural production from lignocellulose is combined with ethanol production from unwashed furfural residues using the SSF method is not clearly outlined in literature. Reducing the severity of the one-stage furfural production step may result in increased ethanol yields since there will be less yeast inhibitors and has potential to improve overall technical and economic outcome, although furfural yield may be reduced. Digestibility and inhibitor concentration levels in

industrial furfural residues also need to be studied to provide a reflection of whether they can be utilised for ethanol co-production without detoxification. Therefore, the aim of this study was to evaluate the effects of one-stage furfural production conditions on the yields of both furfural and ethanol production (from FR) when using the SSF technique without washing (detoxification) or delignification of FR prior to hydrolysis-fermentation.

#### 2 Materials and methods

#### 2.1 Materials

Sugarcane bagasse was sourced locally from sugar mills (Kwa-Zulu Natal, South Africa). Sulphuric acid (98 wt.% H<sub>2</sub>SO<sub>4</sub>) and sodium hydroxide pellets (98 wt.% NaOH) of analytical grade were supplied by Scienceworld (South Africa). Sugarcane bagasse is a lignocellulosic material with potential to improve the overall economics of the sugarmills through production of biochemicals and biofuels. The composition of sugarcane bagasse used was 36% cellulose, 23% hemicellulose, 24% lignin, 4% ash and 6% extractives. Furfural and FR were produced at different conditions using a 2L Büchiglasuster<sup>®</sup> pressure reactor that has Article no.: 45.30148.2200, Serial no.: 4864, and Order no.: 53472. Cellic CTec2<sup>®</sup> and Cellic HTec2<sup>\*</sup> enzymes from Novozymes were used for enzymatic hydrolysis of furfural residues. Industrial FR were obtained from Sezela Illovo sugar mill (South Africa) and RCL. Frozen stock culture of EthanolRed<sup>®</sup> and CelluX<sup>™</sup>4 yeast (*S. cerevisiae*) provided by Lesaffre (Leaf Technologies, France) were used as fermentation microbial yeast strains.

#### 2.2 Experimental design

A face-centred central composite design (CCD) considering temperature and sulphuric acid concentration as independent factors was employed to investigate a range of furfural

production conditions, and their impacts on ethanol production from residues [33, 34]. A temperature range of 170-200 °C and sulphuric acid concentration range of 0-1.0 wt.% as listed in Table 1 were selected, based on previous reports and industrial experience [11, 15, 21, 35]. The experiments were conducted in random order with duplication of the centre point. Analysis of variance (ANOVA) was performed using Statistica® 13.2 software and pvalues below 0.05 were considered to indicate significant effects. Preferred co-production conditions were predicted using the response desirability profiling in Statistica<sup>®</sup> 13.2 software, giving equal weighting to furfural yield (g/100g dry bagasse) and ethanol yield (g/100g dry bagasse) as response variables to be maximised, in response to variations in furfural production conditions [36]. The lowest furfural and ethanol yields (g/100g dry bagasse) obtained in the experiments were allocated as desirability values of zero and highest furfural and ethanol yields (g/100g dry bagasse) were taken as desirability values of one. Each estimated response variable was transformed into desirability values between 0 and 1, and each of the individual desirability values from each of the responses were combined into a single desirability index value (D), geometric mean values computation according to Equation 1 [36].

$$D = (d_1 \times d_2 \times d_3 \times \dots \times d_n)^{1/n}$$

Equation 1

Factors	Low	Intermediate	High		
Temperature (°C)	170	185	200		
H <sub>2</sub> SO <sub>4</sub> wt.% (in solution)	0.0	0.5	1.0		

Table 1: Actual independent factors for the one-stage furfural experiments using a full factorialdesign.

#### 2.3 Furfural production experiments

Sugarcane bagasse was contacted with sulphuric acid in a heated 2L Büchiglasuster® pressure reactor until the target temperature was reached. Furfural vapours were continuously removed from the system through an open valve connected to an outlet pipe immersed in an ice bath to condense the furfural vapour stream. Each experiment was conducted for 90 minutes with initial solids loading of 20 wt.% [15, 35]. Furfural vapour product was extracted at 7 mL/min on average to ensure that 80% of liquid was extracted from the reactor at the end of each experiment based on preliminary studies. Condensed furfural vapour product samples were analysed for furfural, xylose, acetic acid, formic acid and glucose by high performance liquid chromatography (HPLC) (described in analysis section). The solid residues were pressed, to partially remove the absorbed liquids and reduce the yeast inhibition effects of compounds contained in the liquid [32]. The mass of all the remaining solids was measured to determine solids yield and its composition for mass balance calculations. Equations 2 and 3 were used to calculate furfural yield (FF yield) and the combined severity factor (CSF), where theoretical FF is the theoretical yield of furfural (0.727 g furfural/g xylan) [15, 37], t is the residence time in minutes,  $T_H$  is the reactor hydrolysis temperature (°C),  $T_R$  is the reference temperature set at 100°C and pH was the acidity in the reactor at the end of hydrolysis. CSF

is defined to combine the effects of time, temperature and acid dosage in a single function whose value can be correlated to the corresponding products such ethanol yield [28].

$$FF \ yield = \frac{FF \ produced[g]}{theoretical \ FF \ [g]} \times 100\%$$
$$CSF = t. \exp\left(\frac{(T_H - T_R)}{14.73}\right) - pH$$

Equation 2

Equation 3

#### 2.4 Ethanol production from furfural residues

Yeast culture was prepared from a frozen mixed culture in media containing yeast extract (10g/L), peptone (20g/L) and dextrose (50g/L) at 30°C until optical density of 25 at 600nm was reached after 48 hours [38]. The yeast culture was then preconditioned for 24 hours by addition of 3 wt.% hydrolysate to the same flask every 12 hrs until 6 wt.% was reached [28]. The hydrolysate used for preconditioning was obtained from pressing FR produced at the highest severity in furfural experiments. The yeast preconditioning prior to inoculation was conducted to prevent yeast cell death when exposed to synergistic effects of the inhibitors available in the pressed solids [29, 38, 39].

All SSF experiments were conducted at 10 wt.% solids loading using the various pressed FR from the furfural experiments [32, 40]. FR were fed at 5 wt.% at the beginning and a further 5 wt.% on dry basis was added after 24 hours [32]. A 250 mL Erlenmeyer flask was used as a bioreactor and was capped by cotton wool and aluminium foil [22]. NaOH was added to adjust the pH to 5 and a 0.05M citrate buffer was also added into the media to maintain the pH at 5. During sampling, pH was checked and adjusted by addition of NaOH as it decreased to formation of organic acids. Cellic CTec2<sup>®</sup> and Cellic HTec2<sup>®</sup> from Novozymes were contacted

with furfural residue in the flask for two hours prehydrolysis, prior to yeast inoculation with starting absorbency of 2 at 600nm. The total protein content of enzymes used per gram of FR was 26mg, where 19 and 7 mg of proteins were from Cellic CTec2® and Cellic HTec2®, respectively, based on preliminary tests (data not shown) and previous reports [28]. Yeast extract (10g/L) and peptone (20g/L) were added into the SSF flasks to provide nutrition for the yeast. SSF experiments were allowed to run for 120 hours at 37°C and stirring speed of 150 rpm [40]. Temperature of 37°C was considered as a compromise between temperatures suitable for enzymatic hydrolysis (50°C) and fermentation (30°C) [28, 41]. Liquid samples were taken from SSF flasks at different times (0, 16, 24, 40, 48, 64, 72, 88, 112 hrs) with final samples collected after 120 hours. Concentrations of sugars, furfural, HMF (5hydroxymethylfurfural), acetic acid, formic acid and ethanol were determined by HPLC analysis (described in Section 2.5). Vacuum filtration was used to separate the liquid from solid residues at the end of the experiments. The fermentation solid residues were then washed twice in 50 ml tubes using demineralised water filled to the 50 ml mark. Furthermore, the lab FR and those from Sezela Illovo furfural plant and RCL (produced using 10 bar steam and bagasse impregnated with 3 wt.% H<sub>2</sub>SO<sub>4</sub>/dry bagasse) were enzymatically hydrolysed at 10% solids loading to check their digestibility using 38 and 14 mg of proteins from Cellic CTec2<sup>®</sup> and Cellic HTec2<sup>®</sup>, respectively. Enzymatic hydrolysis duration was 96 hrs and the FRs were initially fed at 5 wt.% followed by additional 5 wt.% on dry basis after 24 hours. Inhibitor concentration levels in industrial FR were also evaluated. Fermentation of pressed FR from Sezela Illovo were fermented using M2n previously known as MH1000 [42], while pressed FRs from RCL were fermented using CelluX<sup>™</sup>4 and EthanolRed using the same procedure as lab FRs.

#### 2.5 Analysis

The compositions of feedstock and solid residues were determined using the standard procedures for biomass compositional analysis developed by NREL [43, 44]. A Thermo Separations Product (TSP) high performance liquid chromatography (HPLC) was used to determine the concentrations of furfural, hydroxymethylfurfural (HMF), glucose, cellobiose, xylose, arabinose, acetic acid, formic acid, ethanol and glycerol [43, 44]. The HPLC (Thermo Separations Product) was a Dionex (Dionex, California, USA) 3000 System equipped with a Grace<sup>®</sup> (Hichrom, Berkshire, UK) Prevail Carbohydrate ES Column (250 × 4.6 mm) and a Varian<sup>®</sup> evaporative light scattering detector. HPLC column temperature (80-85°C) and HPLC grade water was used a mobile phase for analysis of the compounds viz., furfural, hydroxymethyl furfural (HMF), glucose, cellobiose, xylose, arabinose, acetic acid, formic acid, ethanol and glycerol [43, 44].

#### **3** Results and Discussion

#### 3.1 Effects of temperature and acid dosage on furfural production from sugarcane

#### bagasse

The experimental conditions and results obtained for one-stage furfural production from sugarcane bagasse are summarised in Table 2. The statistical analysis of the results demonstrated that temperature and sulphuric acid had significant effects on furfural yield (g/100g raw material) in the investigated range (170-200°C, 0-1.0 wt.% H<sub>2</sub>SO<sub>4</sub>), as confirmed by ANOVA reported in Table S1 of the supplementary data. This finding agrees well with literature as Mesa et al. [11] and Sánchez et al. [45] also reported significant effects of temperature and acid loading on furfural yield. The hydrolysis and dehydration processes of

hemicellulose sugars to form furfural and degrade furfural depend on temperature and catalysts used [11, 45], thus, furfural yield was significantly affected.

Overall, furfural yield was in the range of 13-69%, where maximum furfural yield was obtained at 170°C and 0.5 wt.% H<sub>2</sub>SO<sub>4</sub> in 90 minutes as reported Table 2. Furfural yields as high as 68% was also obtained in other studies in shorter residence time at 180°C with addition of 3% of acetic acid and 20 mM of FeCl<sub>3</sub> [37]. Other studies have reported lower furfural yields of 53% when using sugarcane bagasse feed at 175 °C and H<sub>2</sub>SO<sub>4</sub> dosage of 1.25 wt.% on dry feed [11]. The higher furfural yield obtained in this study can be attributed to the longer residence time of 90 minutes compared to 40 minutes in previous studies [11] where 53% furfural yield was achieved. Higher furfural yields of up to 78% were reported at lower temperatures (134°C) and longer residence times (300 min) [46], because furfural degradation reactions are reduced at lower temperatures and acid concentrations [34, 35]. The lowest furfural yield of 13% was obtained at 170°C without sulphuric acid addition, which is comparable to 11% furfural yield achieved in previous studies [47] under similar conditions (170°C, 90 min without acid). Furfural yield is generally lower in the absence of additional acidic catalyst [11, 16, 21]. Higher furfural yields were generally favoured at lower temperatures (170°C) with addition of acid (0.5 wt.% H<sub>2</sub>SO<sub>4</sub>). However, the use of higher acid dosages beyond 0.5 wt.% reduced furfural yield, due to the dominance of furfural degradation reactions [34, 35].

Run	Temperature (°C)	H₂SO₄ (wt.%)	Combined Severity Factor	Formic acid (g/100g dry feed)	Acetic acid (g/100g dry feed)	Furfural (g/100g dry feed)	Furfural theoretical yield %
1	170	0.00	1.50	0.27	1.43	2.28	13.68
2	170	1.00	3.39	1.61	2.60	10.19	61.19
3	200	0.00	2.33	0.14	2.91	5.18	31.14
4	200	1.00	4.26	2.21	2.56	2.52	15.15
5	170	0.50	2.94	0.56	2.21	11.44	68.73
6	200	0.50	3.82	2.00	2.67	6.20	37.24
7	185	0.00	1.94	0.31	2.34	4.83	29.00
8	185	1.00	3.88	2.38	2.54	5.34	32.07
9 (C)	185	0.50	3.58	2.04	2.71	8.40	50.47
10 (C)	185	0.50	3.58	2.02	2.67	8.12	48.79

Table 2: Furfural production conditions with corresponding average concentration of main products and furfural yield as a percentage of theoretical yield.

NB: Feedstock composition: 36% cellulose, 23% hemicellulose, 24% lignin, 4% ash and 6%; wt.%  $H_2SO_4$  is in initial solution

#### 3.2 Effects of furfural production conditions on formation of organic acids

Furfural production is generally accompanied by formation of acetic acid, generated from acetyl groups contained in hemicelluloses of lignocellulosic materials. The effects of furfural reactor temperature and acid dosage on the average acetic acid concentration in the furfural product stream are shown in **Fig. 1a**. The lowest amount of acetic acid (4.36 g/L) was formed at the least severe furfural production conditions (170°C and 0% H<sub>2</sub>SO<sub>4</sub>), while acetic acid formation remained stable at 6.9-7.9 g/L at the other investigated conditions (**Fig. 1a**), which is similar to the trend reported by García-Domínguez et al. [48]. The least severe conditions were therefore not sufficient for complete liberation of the acetyl groups from the hemicelluloses [48, 49]. The variations in acetic acid concentrations from 6.9 to 7.9 g/L may be attributed to the differences in vapour stripping capabilities of the furfural reactor when operated at different temperatures.

The extent of formic acid formation (5.52-6.51 g/L) was larger at higher temperatures (185-200°C) in the presence of sulphuric acid (**Fig. 1b**). Higher concentration of formic acid (5.52-

6.51 g/L) at higher temperatures in the presence of sulphuric acid (**Fig. 1b**) is explained by degradation of sugars and furfural degradation to formic acid through the hydrolytic fission of the aldehyde group of furfural [17]. The low cellulose content (<12 wt.%) of solid residues of furfural production process (provided in Table 3) at higher temperatures in the presence of sulphuric acid supports the occurrence of cellulose degradation to glucose and subsequently to formic acid and levulinic acid [15, 50, 51].



Fig. 1: Effects of sulphuric acid dosage and temperature on a) acetic acid and b) formic acid concentration in furfural product.

#### 3.3 Effects of furfural production conditions on ethanol co-production from residues

The solid residues obtained from furfural production suffered significant degradation of cellulose of up to 89% of cellulose present in raw bagasse removed by the most severe process conditions as reported in Table 3, which limits ethanol co-production from furfural residues in a sequential biorefinery. The cellulose content was generally higher for FR produced without the addition of acid and this concurs with compositional analysis of autohydrolysis industrial FR (Table 4). However, at the most, 22% of cellulose in raw bagasse

was preserved in residues produced with the addition of catalyst, except for residues produced at 170°C and 0.5 wt.% H<sub>2</sub>SO<sub>4</sub>, where FRs contained 53% wt.% cellulose (~80% cellulose recovery) (Table 3, Run 5). Traditional furfural technologies that use sulphuric acid (1.5wt.%) as catalyst operated at 175°C for 120 minutes end up with FR that contain about 15 wt.% cellulose [11]. This study shows that the severity of the furfural process with 90 minutes residence at temperature of 170°C with addition of 0.5 wt.% H<sub>2</sub>SO<sub>4</sub> preserved the cellulose fraction as indicated by the resulting FR that had 53% cellulose (Table 3). Similar studies also reported that FR produced at 175°C and 1.25 wt.% H<sub>2</sub>SO<sub>4</sub> in a furfural process with 40 minutes residence time contained of 48 wt.% cellulose, showing ability of the acid catalysed furfural process to preserve cellulose at shorter residence time of 40 minutes [11]. In addition to the degradation of cellulose, the presence of yeast inhibitors also affected the final ethanol yields.

The use of inhibitor-resistant yeast resulted in higher ethanol yields even from FRs obtained at higher severities where maximum furfural was obtained. For instance, ethanol yield was 96% when using CelluX<sup>™</sup>4 to ferment FRs from which maximum furfural yield of 69% was obtained, but only reached 77% when EthanolRed<sup>®</sup> was employed as shown in **Fig. 2**. The use of highly inhibitor-resistant yeast allows for improved yeast performance even under stressful environments [29, 31]. Ethanol yields were higher (68-95%) at lower severities (CSF: 1.49-2.94), whereas ethanol yield decreased to 13-63% at higher severities (CSF: 3.38-4.25) as shown in **Fig. 2**. In the case of highly inhibitory FRs from CSF of 3.88, fermentation using EthanolRed<sup>®</sup> yeast strain resulted in 13% ethanol yield (2) due to yeast cell death caused by inhibitors as evidenced by glucose accumulation of 6 g/L. Furthermore, FRs from CSF of 3.88 were the only batch in which 50% of the glucose released by enzymatic hydrolysis remained unused (Table 3).

The yeast dealt with the inhibition caused by organic acids by increasing its redox capacity available, as demonstrated by an increase in glycerol production (Table 3). It is estimated that 13-18% of the glucose released from FRs during SSF were utilized for the formation of by-products such as glycerol, which is higher than typical glycerol formation of 4-10% of glucose [52], indicating an increase in cytosolic redox balancing to provide metabolic capacity for the detoxification of organic acids [53]. Although the SSF cultures were maintained at pH of 5 to minimize the toxicity of organic acids [29, 31], yeast inhibition above certain thresholds of these acids is inevitable regardless of pH [29, 30].

While the yeasts were able to handle the inhibition caused by organic acids through metabolic conversion to remove them from the culture broth, the yeast could only remove limited amounts of the furans (furfural and HMF) present in the FR (Table 3). Specifically, the starting concentrations of HMF in SSF cultures increased in the CSF range of 1.50-2.94 and the HMF levels were below HPLC detection limits above CSF range of 1.50-2.94, possibly due to HMF degradation to levulinic and formic acids [35, 51]. The yeasts capability to convert furfural and HMF to their corresponding alcohols, furfuryl alcohol and hydroxymethyl furfuryl alcohol, which are less inhibitory [31, 54], was demonstrated by the complete removal of furfural from SSF flasks, while much reduced concentrations of HMF remained at the end of each run.

In addition to organic acids and furans, pseudo-lignin formed at higher severities (CSF>2.94) also contributed towards yeast inhibition and the corresponding low ethanol yields from sugars of 13-68%. The additional lignin formed at higher severities (CSF>2.94) constituted 45-52% of furfural residues mass (Table 3). Higher severity conditions are associated with elevated temperatures ( $\geq$ 185°C) and acid concentrations ( $\geq$ 0.5 wt.% H<sub>2</sub>SO<sub>4</sub>), therefore, the furfural and sugar degradation reactions that form pseudo-lignin are favoured at higher

severities [55]. Dilute acid pretreatment at higher severities has been shown to result in pseudo-lignin formation, which is known to cause enzymatic and microbial inhibition [55]. Other studies report that even at low severities (160°C, 0.1 M H<sub>2</sub>SO<sub>4</sub>, 2.5 min) certain amounts of pseudo-lignin can form and deposit onto cellulose, thereby reducing cellulose accessibility to enzymes and yeast inhibition [56].

While low severity conditions (CSF<2.94) preserve cellulose and result in higher ethanol mass produced (13.02-17.32 g/100g raw bagasse), the corresponding furfural yields were below 35% (Table 3), which is less than 50% furfural yields achieved at industrial scale [9]. The extent of pentose sugar conversion to furfural at low severities which correspond to conditions that maximise ethanol yield is low [35, 46]. Higher furfural yields are recommended in furfural and ethanol co-production biorefineries to achieve higher furfural production rates and sales [9], considering that cellulosic ethanol is also cost intensive and tends to need subsidy [11, 13].

Furfural Residues										
Run	1	2	3	4	5	6	7	8	9	10
Cellulose (%)	61.14	11.80	55.72	5.83	52.59	7.12	46.21	6.80	6.89	6.91
Hemicellulose (%)	7.32	6.26	3.21	6.30	3.49	6.29	12.08	6.30	6.64	6.64
Total Lignin (%)	31.54	81.93	41.07	87.87	43.91	86.59	41.71	86.90	86.47	86.45
% of acid insoluble material formed	0.00	45.12	0.00	81.93	1.75	46.63	0.00	47.11	49.26	48.65
Furfural produced (g/100g dry	2 20	10.10	F 10	2 5 2	11 14	6.20	4 02	F 24	0 40	0 1 2
bagasse)	2.28	10.19	5.18	2.52	11.44	6.20	4.85	5.34	8.40	8.12
FF yield	13.68	61.19	31.14	15.15	68.73	37.24	29.00	32.07	50.47	48.79
Combined severity factor (CSF)	1.50	3.39	2.33	4.26	2.94	3.82	1.94	3.88	3.58	3.58
	Enzyn	natic soli	d hydrol	ysis at 10	)% solids	;				
Glucose (g/L)	63.01	16.69	65.12	12.67	37.38	12.76	62.18	12.11	12.83	13.86
Xylose (g/L)	17.79	6.88	7.08	7.14	6.46	6.72	9.01	6.75	6.28	7.06
Concentration of inhibitors in 5% solids after 2 hours prehydrolysis										
Run	1	2	3	4	5	6	7	8	9	10
Formic acid (g/L)	0.88	1.80	0.87	1.20	1.37	1.36	0.87	1.50	1.63	1.63
Acetic acid (g/L)	1.02	0.60	0.81	0.53	0.67	0.62	0.90	0.59	0.60	0.60
HMF (g/L	nd	0,10	0,28	nd	0,38	nd	0.13	nd	nd	nd
Furfural (g/L)	0.13	nd	nd	nd	0.08	nd	0.17	nd	nd	nd
	Ferme	entation	using Eth	nanolRed	l® in SSF					
Run	1	2	3	4	5	6	7	8	9	10
Glucose in residue (g/L)	2.09	3.44	0.70	0.00	0.60	0.00	1.83	6.08	0.00	0.00
Xylose in residue (g/L)	6.36	1.24	0.51	0.00	0.00	0.00	2.51	5.07	0.00	0.00
EtOH concentration (g/L)	28.11	6.03	31.99	5.29	17.21	4.71	32.03	1.33	5.24	5.31
EtOH yield %	68.09	50.04	86.70	52.24	76.83	47.30	88.05	13.84	53.69	49.69
EtOH produced (g/100g dry bagasse)	13.02	4.43	17.19	4.15	9.57	3.29	16.74	1.30	4.01	3.99
Glycerol (g/L)	0.00	2.37	1.90	1.61	2.59	1.63	1.72	0.00	1.88	1.90
Fermentation using CelluX™4 in SSF										
Run	1	2	3	4	5	6	7	8	9	10
Glucose in residue (g/L)	0.59	2.95	0.00	0.59	0.60	0.00	1.20	0.00	0.00	0.00
Xylose in residue (g/L)	1.06	0.00	0.00	0.00	0.00	0.00	0.81	0.00	0.00	0.00
EtOH concentration (g/L)	32.79	6.35	32.52	5.99	21.46	4.71	32.32	6.14	5.88	6.10
EtOH yield %	79.43	52.75	88.14	59.16	95.80	47.35	88.84	63.74	60.25	57.03

## Table 3: Fermentation results of furfural residues from laboratory furfural production at different conditions using EthanolRed<sup>®</sup> and CelluX<sup>™</sup>4.

FF refers to furfural; EtOH refers to ethanol; HMF refers to 5-Hydroxymethylfurfural; nd stands for not detected

17.32

2.60

4.37

1.74

11.58

2.80

3.31

1.67

16.81

2.44

4.11

1.91

4.25

2.34

4.30

2.36

4.62

2.46

14.20

2.22

EtOH produced (g/100g dry bagasse)

Glycerol (g/L)



Fig. 2: Ethanol yield from sugars released by enzymatic hydrolysis of furfural residues produced at different combined severity factors (CSF) when using EthanolRed<sup>®</sup> and CelluX<sup>™</sup>4.

As part of the study, industrial FRs were successfully enzymatically hydrolysed and converted to ethanol without the need for detoxification and delignification. Glucan conversion of the autocatalysed industrial FRs was 79% and the glucan conversion of the acid catalysed industrial residues was higher with values of at least 89% (Table 4). While the acid catalysed residues were more digestible, their lower cellulose content (44%) resulted in similar amounts of sugars available for ethanol production compared to autocatalysed FRs, which had higher cellulose content (57 wt.%) (Table 4). The industrial acid catalysed FR were produced at less severe conditions in comparison to traditional furfural process [11]. Thus, the industrial FR from acid catalysed process could be digested and converted to ethanol without the need for delignification to render them digestible [25–27]. Higher severity conditions (CSF>2.94) resulted in larger amount of acid insoluble material compared to lignin in raw bagasse (Table 3). The less severe acidic conditions applied in this study reduced the formation of pseudo-lignin, thus avoiding the associated inhibition of enzymatic hydrolysis and microbial conversions [27, 55].

Industrial furfural residual solids produced by autocatalytic process caused less inhibition to yeast cells in comparison to solids from acid catalysed furfural process. Initial concentration levels of acetic and formic acid in 5% acid catalysed solids reached up to 9.2 g/L and 1.8 g/L, respectively, whereas the acetic and formic acid concentration levels only reached 1.0 g/L and 0.9 g/L in autocatalysed furfural residues, respectively (Table 4). Both formic and acetic acid reduces yeast cell performance and may cause yeast cell death at certain thresholds [29, 31], but formic acid causes greater toxicity than acetic acid [39]. In general, less severe furfural processes are preferred when considering ethanol co-production, since less severe furfural

processes result in low concentration levels of yeast inhibitors - provided that an acceptable

furfural yield can be maintained under these less severe conditions.

## Table 4: Enzymatic hydrolysis of furfural residues from furfural demonstration plant and industrialplant.

	Industrial furfural residues used as SSF feed									
	Sezela Residue	Batch 39	Batch 40	Batch 42	Batch 48	Batch 51	Batch 55			
Cellulose (%)	56.65	22.00	11.95	43.22	44,45	29.66	22.29			
Hemicellulose (%)	nd	nd	nd	nd	nd	nd	nd			
Lignin (%)	43.35	65.09	82.83	35.86	35.63	54.05	65.96			
Ash (%)	nd	10.50	8.77	6.28	8.51	10.29	9.47			
	Enzymatic hydrolysis at 5% solids									
	Sezela Residue	Batch 39	Batch 40	Batch 42	Batch 48	Batch 51	Batch 55			
Glucose (g/L)	24.86	14.30	8.33	26.68	24.94	18.31	13.76			
Xylose (g/L)	1.00	2.50	2.64	3.28	2.91	2.50	3.71			
Formic acid (g/L)	nd	1.13	1.34	nd	nd	nd	1.15			
Acetic acid (g/L)	0.61	6.74	9.24	3.00	nd	1.87	6.19			
HMF (g/L	0.46	0.28	0.07	0.39	0.06	0.20	0.26			
Furfural (g/L)	nd	nd	nd	0.08	nd	nd	nd			
	Fermentation									
	using M2n	Fe	ermentation u	ising Ethano	IRed <sup>®</sup> with 1	0% solids				
	Sezela Residue	Batch 39	Batch 40	Batch 42	Batch 48	Batch 51	Batch 55			
% Ethanol yield (g/(0,511 g sugars))	89.77	99.55	83.78	94.99	88.73	92.58	85.66			
		Fermentation using CelluX <sup>™</sup> 4 with 10% solids								
		Batch 39	Batch 40	Batch 42	Batch 48	Batch 51	Batch 55			
% Ethanol yield (g/(0,511 g sugars))		93.99	84.00	90.46	89.49	96.07	89.67			

nd stands for not detected

#### 3.4 Optimum feedstock conversion to furfural and ethanol

The preferred conditions for furfural and ethanol co-production result in a compromise of the yields of the two products. The preferred furfural and ethanol co-production conditions based on desirability plot results were 170°C and 0.25 wt.% H<sub>2</sub>SO<sub>4</sub>, where furfural produced is 7.64g/100g of dry feed (~50% yield) with ethanol reaching 9.86 and 10.91g/100g of dry feed when using EthanolRed<sup>®</sup>(~47% yield) and CelluX<sup>™</sup>4 (~57% yield), respectively as shown in **Fig. 3**. Detailed desirability plots are provided in **Fig. S1-S2** of supplementary data file. The highest

furfural produced was 11.44g/100g of dry raw biomass and was obtained at medium severity conditions under acid catalysis (170°C and 0.5 wt.%  $H_2SO_4$ , CSF = 2.94), whereas the highest mass of ethanol produced (17.19-17.32g/100g dry raw bagasse) using EthanolRed<sup>\*</sup> and CelluX<sup>™</sup>4 was obtained from residues produced by autohydrolysis (CSF=2.33) at 200°C. Higher severity conditions (CSF>2.94) degraded cellulose, thus, overall mass of ethanol produced from raw bagasse to ethanol was 1.30-11.58g/100g of raw dry bagasse. Studies report that cellulose degradation during furfural process can reach 40 to 50% [13], thus, ethanol mass produced indicating utilisation of 50% of cellulose available in the raw bagasse is reasonable.



Fig. 3: Preferred furfural conditions for furfural and ethanol co-production indicated by desirability values and mass of furfural and ethanol (EthanolRed<sup>®</sup> and CelluX<sup>™</sup>4) produced per 100g of raw bagasse.

#### 4 Conclusions

Conditions that maximised furfural yield resulted in low ethanol mass produced per mass of raw feedstock due to yeast inhibition caused by organic acids, furans, pseudo-lignin and cellulose degradation. The use of more inhibitor resistant yeast allowed achieving higher ethanol yields in comparison to yeast with low inhibitor tolerance. Higher ethanol yields were achieved from FRs produced at low severities, but corresponding furfural yields were below industrial yields. Conditions suitable for optimal co-production of furfural and ethanol (170°C
and 0.25 wt.% H<sub>2</sub>SO<sub>4</sub>) resulted in a yield compromise of both products. Subsequent studies focused on economic impact of furfural and ethanol yield are required to determine overall profitability. Future studies should explore various conditions for the two-stage furfural process that produce digestible solids with minimal cellulose degradation to allow high yields of ethanol and furfural.

#### Acknowledgements

We thank National Research Fund (South Africa) and Sugar Milling Research Institute for support. The Sugarcane Technology Enabling Programme for Bioenergy (STEP-Bio), a public: a private partnership between the South African sugarcane processing industry and the Department of Science and Technology (DST) Sector Innovation Fund (SIF) is acknowledged for partial support. We extend gratitude to Novozymes for providing us with enzymes, Lesaffre (Leaf Technologies, France) for providing us with yeast strains, Illovo Sezela for providing us with furfural residues and technical advice, and RCL for providing us with furfural residues. Finally yet importantly, we also thank Analytical Lab team of the Department of Process engineering, Stellenbosch University.

# Declaration

The authors declare that they have no conflict of interest.

#### References

- Panahi HSK, Dehhaghi M, Kinder JE, Ezeji TC (2019) A review on green liquid fuels for the transportation sector : a prospect of microbial solutions to climate change.
   Biofuel Res J 23:995–1024. https://doi.org/10.18331/BRJ2019.6.3.2
- Tabatabaei M, Mortaza A, Valijanian E, et al (2020) A comprehensive review on recent biological innovations to improve biogas production, Part 1 : Upstream strategies.
   Renew Energy 146:1204–1220.

https://doi.org/https://doi.org/10.1016/j.renene.2019.07.037

- Machineni L (2020) Lignocellulosic biofuel production: review of alternatives. Biomass
   Convers Biorefinery 10:779–791. https://doi.org/10.1007/s13399-019-00445-x
- Ho MC, Ong VZ, Wu TY (2019) Potential use of alkaline hydrogen peroxide in lignocellulosic biomass pretreatment and valorization – A review. Renew Sustain Energy Rev 112:75–86. https://doi.org/10.1016/j.rser.2019.04.082
- 5. Biddy MJ, Scarlata C, Christopher K (2016) Chemicals from Biomass: A Market Assessment of Bioproducts with Near-Term Potential
- Bohre A, Dutta S, Saha B, Abu-omar MM (2015) Upgrading Furfurals to Drop-in Biofuels: An Overview. ACS Sustain Chem Eng 3:1263–1277. https://doi.org/10.1021/acssuschemeng.5b00271
- Dalvand K, Rubin J, Gunukula S, et al (2018) Economics of biofuels : Market potential of furfural and its derivatives. Biomass and Bioenergy 115:56–63. https://doi.org/10.1016/j.biombioe.2018.04.005
- Chen H, Qin L, Yu B (2015) Furfural production from steam explosion liquor of rice straw by solid acid catalysts (HZSM-5). Biomass and Bioenergy 73:77–83. https://doi.org/10.1016/j.biombioe.2014.12.013

- Cai CM, Zhang T, Kumar R, Wyman CE (2014) Integrated furfural production as a renewable fuel and chemical platform from lignocellulosic biomass. J Chem Technol Biotechnol 89:2–10. https://doi.org/10.1002/jctb.4168
- 10. Lavarack BP, Griffin GJ, Rodman D (2002) The acid hydrolysis of sugarcane bagasse hemicellulose to produce xylose, arabinose, glucose and other products. Biomass and Bioenergy 23:367–380
- Mesa L, Morales M, González E, et al (2014) Restructuring the processes for furfural and xylose production from sugarcane bagasse in a biorefinery concept for ethanol production. Chem Eng Process Process Intensif 85:196–202. https://doi.org/10.1016/j.cep.2014.07.012
- Lee CBTL, Wu TY (2020) A review on solvent systems for furfural production from lignocellulosic biomass. Renew Sustain Energy Rev 137:110172. https://doi.org/10.1016/j.rser.2020.110172
- Rosales-Calderon O, Arantes V (2019) A review on commercial- scale high-value products that can be produced alongside cellulosic ethanol. Biotechnol Biofuels 12:1– 58. https://doi.org/10.1186/s13068-019-1529-1
- Farzad S, Mandegari MA, Guo M, et al (2017) Multi-product biorefineries from
   lignocelluloses: A pathway to revitalisation of the Sugar Industry? Biotechnol Biofuels
   10:1–24. https://doi.org/10.1186/s13068-017-0761-9
- 15. Zeitsch KJJ (2000) The chemistry and technology of furfural and its many by-products
- Dashtban M, Technologies A, Dashtban M (2012) PRODUCTION OF FURFURAL:
   OVERVIEW AND CHALLENGES. J Sci Technol For Prod Process 2:44–53
- 17. Danon B, Marcotullio G, De Jong W (2013) Mechanistic and kinetic aspects of pentose dehydration towards furfural in aqueous media employing homogeneous catalysis.

Green Chem 1–16. https://doi.org/10.1039/b000000x

- Cardona CA, Quintero JA, Paz IC (2010) Production of bioethanol from sugarcane bagasse: Status and perspectives. Bioresour Technol 101:4754–4766. https://doi.org/10.1016/j.biortech.2009.10.097
- 19. Steinbach D, Kruse A, Sauer J (2017) Pretreatment technologies of lignocellulosic biomass in water in view of furfural and 5-hydroxymethylfurfural production- A review. Biomass Convers Biorefinery. https://doi.org/10.1007/s13399-017-0243-0
- Silva JFL, Selicani MA, Junqueira TL, et al (2017) Integrated furfural and first generation bioethanol production: Process simulation and technoeconomic analysis.
   Brazilian J Chem Eng 34:623–634. https://doi.org/10.1590/0104-6632.20170343s20150643
- 21. Avci A, Saha BC, Kennedy GJ, Cotta MA (2013) High temperature dilute phosphoric acid pretreatment of corn stover for furfural and ethanol production. Ind Crops Prod 50:478–484. https://doi.org/10.1016/j.indcrop.2013.07.055
- Yoo CG, Kuo M, Kim TH (2012) Ethanol and furfural production from corn stover using a hybrid fractionation process with zinc chloride and simultaneous saccharification and fermentation (SSF). Process Biochem 47:319–326. https://doi.org/10.1016/j.procbio.2011.11.018

 Shi X, Zhao B, Zhou H, et al (2019) Direct Saccharification and Fermentation for High Glucose and Ethanol Production from Non-Detoxified Furfural Residue Without Any Pretreatment. Energy Technol Environ Sci 4:7844–7850. https://doi.org/10.1002/slct.201901367

24. Wang K, Yang H, Chen Q, Sun R cang (2013) Influence of delignification efficiency with alkaline peroxide on the digestibility of furfural residues for bioethanol production.

Bioresour Technol 146:208–214. https://doi.org/10.1016/j.biortech.2013.07.008

- 25. Xing Y, Bu L, Sun D, et al (2016) Enhancement of high-solids enzymatic hydrolysis and fermentation of furfural residues by addition of Gleditsia saponin. FUEL 177:142–147. https://doi.org/10.1016/j.fuel.2016.03.024
- 26. Bu L, Tang Y, Xing Y, et al (2014) Comparison of hydrophilic variation and bioethanol production of furfural residues after delignification pretreatment. Biosci Biotechnol Biochem 78:1435–1443. https://doi.org/10.1080/09168451.2014.921556
- Ji L, Zheng T, Zhao P, et al (2016) Ethanol production from a biomass mixture of furfural residues with green liquor-peroxide saccarified cassava liquid. BMC
   Biotechnol 16:1–11. https://doi.org/10.1186/s12896-016-0278-5
- 28. Mokomele T, Sousa C, Balan V, et al (2018) Ethanol production potential from AFEX <sup>™</sup> and steam exploded sugarcane residues for sugarcane biorefineries. Biotechnol Biofuels 11:1–21. https://doi.org/10.1186/s13068-018-1130-z
- 29. Watanabe K, Tachibana S, Konishi M (2019) Modeling growth and fermentation inhibition during bioethanol production using component pro fi les obtained by performing comprehensive targeted and non-targeted analyses. Bioresour Technol 281:260–268. https://doi.org/10.1016/j.biortech.2019.02.081
- Wang X, Fai Y, Li Y, et al (2017) Inhibitory e ff ects of phenolic compounds of rice straw formed by sacchari fi cation during ethanol fermentation by Pichia stipitis.
   Bioresour Technol 244:1059–1067. https://doi.org/10.1016/j.biortech.2017.08.096
- Xu K, Seo Y, Li J, Li C (2019) Resistance mechanisms and reprogramming of microorganisms for e ffi cient biore fi nery under multiple environmental stresses.
   Synth Syst Biotechnol J 4:92–98. https://doi.org/10.1016/j.synbio.2019.02.003
- 32. He J, Zhang W, Liu X, et al (2016) Optimization of prehydrolysis time and substrate

feeding to improve ethanol production by simultaneous saccharification and fermentation of furfural process residue. J Biosci Bioeng 122:563–569. https://doi.org/10.1016/j.jbiosc.2016.04.012

- 33. Pabari RM, Ramtoola Z (2012) Application of face centred central composite design to optimise compression force and tablet diameter for the formulation of mechanically strong and fast disintegrating orodispersible tablets. Int J Pharm 430:18–25. https://doi.org/10.1016/j.ijpharm.2012.03.021
- Yemiş O, Mazza G (2011) Acid-catalyzed conversion of xylose, xylan and straw into furfural by microwave-assisted reaction. Bioresour Technol 102:7371–7378.
   https://doi.org/10.1016/j.biortech.2011.04.050
- Bamufleh HS, Alhamed YA, Daous MA (2013) Furfural from midribs of date-palm trees by sulfuric acid hydrolysis. Ind Crop Prod 42:421–428. https://doi.org/10.1016/j.indcrop.2012.06.008
- 36. Mesa L, Martínez Y, Barrio E, González E (2017) Desirability function for optimization of Dilute Acid pretreatment of sugarcane straw for ethanol production and preliminary economic analysis based in three fermentation configurations. Appl Energy 198:299–311. https://doi.org/10.1016/j.apenergy.2017.03.018
- 37. Mao L, Zhang L, Gao N, Li A (2012) FeCl 3 and acetic acid co-catalyzed hydrolysis of corncob for improving furfural production and lignin removal from residue. Bioresour Technol 123:324–331. https://doi.org/10.1016/j.biortech.2012.07.058
- Zhao M, Shi D, Lu X, et al (2019) Ethanol fermentation from non-detoxified lignocellulose hydrolysate by a multi-stress tolerant yeast Candida glycerinogenes mutant. Bioresour Technol 273:634–640.

https://doi.org/10.1016/j.biortech.2018.11.053

- Guo Z, Olsson L (2016) Physiological responses to acid stress by Saccharomyces cerevisiae when applying high initial cell density. 2 FEMS Yeast Res 16:1–11. https://doi.org/10.1093/femsyr/fow072
- 40. Unrean P, Khajeeram S, Laoteng K (2016) Systematic optimization of fed-batch simultaneous saccharification and fermentation at high-solid loading based on enzymatic hydrolysis and dynamic metabolic modeling of Saccharomyces cerevisiae. Appl Microbiol Biotechnol 100:2459–2470. https://doi.org/10.1007/s00253-015-7173-1
- Boshoff S, Gottumukkala LD, Rensburg E Van, Görgens J (2016) Paper sludge ( PS ) to bioethanol: Evaluation of virgin and recycle mill sludge for low enzyme , high-solids fermentation. Bioresour Technol 203:103–111. https://doi.org/10.1016/j.biortech.2015.12.028
- Favaro L, Viktor MJ, Rose SH, et al (2015) Consolidated bioprocessing of starchy substrates into ethanol by industrial Saccharomyces cerevisiae strains secreting fungal amylases. Biotechnol Bioeng 112:1751–1760.

https://doi.org/10.1002/bit.25591

- 43. Sluiter A, Hames B, Ruiz R, et al (2012) Determination of Structural Carbohydrates and Lignin in Biomass
- Raman JK, Gnansounou E (2015) Furfural production from empty fruit bunch A biorefinery approach. Ind Crops Prod 69:371–377.
   https://doi.org/10.1016/j.indcrop.2015.02.063
- 45. Sánchez C, Serrano L, Andres MA, Labidi J (2013) Furfural production from corn cobs autohydrolysis liquors by microwave technology. Ind Crops Prod 42:513–519. https://doi.org/10.1016/j.indcrop.2012.06.042

- Vázquez M, Oliva M, Téllez-Luis SJ, Ramírez JA (2007) Hydrolysis of sorghum straw using phosphoric acid: Evaluation of furfural production. Bioresour Technol 98:3053–3060. https://doi.org/10.1016/j.biortech.2006.10.017
- 47. Vallejos ME, Felissia FE, Kruyeniski J, Area MC (2015) Kinetic study of the extraction of hemicellulosic carbohydrates from sugarcane bagasse by hot water treatment. Ind Crops Prod 67:1–6. https://doi.org/10.1016/j.indcrop.2014.12.058
- García-Domínguez MT, García-Domínguez JC, Feria MJ, et al (2013) Furfural
   production from Eucalyptus globulus: Optimizing by using neural fuzzy models. Chem
   Eng J 221:185–192. https://doi.org/10.1016/j.cej.2013.01.099
- Aguilar R, Ramírez JA, Garrote G, Vázquez M (2002) Kinetic study of the acid hydrolysis of sugar cane bagasse. J Food Eng 55:309–318. https://doi.org/10.1016/S0260-8774(02)00106-1
- Li H, Wang X, Liu C, et al (2016) An efficient pretreatment for the selectively hydrothermal conversion of corncob into furfural: The combined mixed ball milling and ultrasonic pretreatments. Ind Crops Prod 94:721–728. https://doi.org/10.1016/j.indcrop.2016.09.052
- 51. Dussan K, Girisuta B, Haverty D, et al (2013) Kinetics of levulinic acid and furfural production from Miscanthus×giganteus. Bioresour Technol 149:216–224. https://doi.org/10.1016/j.biortech.2013.09.006
- Albers E, Larsson C, Liden G, et al (1996) Influence of the Nitrogen Source on Saccharomyces cerevisiae Anaerobic Growth and Product Formation. Appl Environ Microbiol 62:3187–3195
- 53. Wang Z, Zhuge J, Fang H, Prior BA (2001) Glycerol production by microbial fermentation : A review. Biotechnol Adv 19 19:201–223

- 54. Hanly TJ, Henson MA (2014) Dynamic Model-Based Analysis of Furfural and HMF
   Detoxification by Pure and Mixed Batch Cultures of S . cerevisiae and S . stipitis.
   Biotechnol Bioeng 111:272–284. https://doi.org/10.1002/bit.25101
- 55. Hu F, Jung S, Ragauskas A (2012) Pseudo-lignin formation and its impact on enzymatic hydrolysis. Bioresour Technol 117:7–12.
   https://doi.org/10.1016/j.biortech.2012.04.037
- 56. Shinde SD, Meng X, Kumar R, Ragauskas AJ (2018) Recent advances in understanding the pseudo-lignin formation in a lignocellulosic biorefinery. Green Chem 20:2192– 2205. https://doi.org/10.1039/c8gc00353j

# Chapter 5: Techno-economics of one-stage furfural and ethanol coproduction

**Chapter submitted in:** Industrial Crops and Products, Cite Score: 6.9, Impact Factor: 4.244

Title: Techno-economic assessment of one-stage furfural and cellulosic ethanol co-production from sugarcane bagasse and harvest residues feedstock mixture
Authors: Rhulani N. Ntimbani, Somayeh Farzad, Johann F. Görgens
Declaration: This chapter has been published in Industrial Crops and Products Journal. It has been reproduced in this dissertation as is with the permission of Elsevier.

# Objectives of this chapter in dissertation and findings

The research objectives outlined as part of Contribution 2 are addressed in this chapter of the dissertation. The study was focused on evaluating the technical and economic aspects of an energy self-sufficient biorefinery employing the one-stage furfural process, with ethanol co-production from residual lignocellulose biomass produced. The process flowsheet of the one-stage furfural process and ethanol co-production were developed using furfural and ethanol yield data obtained in Chapter 4 (Contribution 1). The study included evaluating the potential of the one-stage furfural process in lowering minimum selling price of ethanol.

Furfural production is economically more attractive than ethanol production and ethanol co-production does not improve furfural economics. Ethanol and furfural coproduction is more economically attractive than ethanol production and better results could be expected in a system with fewer limitations in energy supply. Improvement in minimum ethanol selling price required in furfural and ethanol co-production was impeded by lower ethanol yields and production rates negatively influenced by energy demands that were supplied by a portion of feedstock. The most promising one-stage furfural and ethanol integrated biorefinery was compared to the integrated two-stage furfural and ethanol biorefinery as part of this study in Chapter 6.

# Declaration by the candidate:

With regards to Chapter 5, page numbers 106-143 of this dissertation, the nature and scope

of my contributions were as follows:

Nature of contribution	Extent of contribution (%)
Simulation work planning	95
Executing simulations and techno-economics	100
Interpretation of results	90
Writing the chapter	100

The following co-authors have contributed to Chapter 5 pages 106-143 in the dissertation in the following manner:

Name	E-mail address	Nature of contribution	Extent of contribution (%)
		Simulation work	5
Somayeh Farzad	<u>sfarzad@sun.ac.za</u>	<ul><li>planning</li><li>Interpretation of results</li></ul>	5
		<ul> <li>Reviewing chapter</li> </ul>	50
Johann Ferdinand Görgens	jgorgens@sun.ac.za	<ul> <li>Interpretation of results</li> </ul>	5
		<ul> <li>Reviewing chapter</li> </ul>	50

Candidate signature:....

Date:....

Declaration with signature in possession of candidate and supervisor.

# **Declaration by co-authors**

All authors read and approved this manuscript and hereby confirm that:

I. The declaration above accurately reflects the nature and extent of the contributions of the candidates and co-authors to Chapter 5, page numbers 106-143 in the dissertation,

II. No other authors contributed to Chapter 5, page numbers 106-143 in the dissertation beside those specified above, and

III. Potential conflicts of interest have been revealed to all interested parties and that are necessary arrangements have been made to use the material in Chapter 5 of the dissertation.

# Techno-economic assessment of one-stage furfural and cellulosic ethanol co-production from

#### sugarcane bagasse and harvest residues feedstock mixture

Rhulani N. Ntimbani, Somayeh Farzad\*, Johann F. Görgens

Department of Process Engineering, Stellenbosch University, Private Bag X1, Stellenbosch 7602, South Africa

### Highlights

- One-stage furfural coproduction improved the overall bioethanol economics
- Furfural-ethanol biorefinery economics are less prone to product price fluctuations
- Furfural-ethanol biorefinery profitability is less dependent on electricity sales
- Energy demands limited one-stage furfural and ethanol co-production profitability

#### Abstract

Co-production of furfural and ethanol from mixture of sugarcane bagasse and harvest residues in a biorefinery annexed to a sugar mill was investigated. The study considered energy self-sufficient scenarios producing furfural-only (scenario 1), ethanol-only (scenario 2) and integrated furfural-ethanol co-production at a range of operating conditions (scenarios 3-7). Scenario 1 was based on the industrial furfural process conditions (180°C), which was replaced with steam explosion pretreatment at 205°C in the ethanol-only Scenario 2. Furfural process conditions of Scenarios 3,4 and 6 were autocatalytic at 170°C, 200°C and 185°C, respectively, while the furfural conditions with 0.5wt% H<sub>2</sub>SO<sub>4</sub> at 170°C and 185°C were applied for Scenarios 5 and 7, respectively. All investigated scenarios were simulated in Aspen

Plus® V8.8, with economic viability expressed by internal rate of return (IRR). The integrated furfural and ethanol biorefinery (Scenario 5) was more profitable than ethanol-only production (scenario 2) as indicated by 12.78% and 10.18% IRR, respectively. However, furfural-only biorefinery was the most profitable with IRR of 12.92% as it was associated with lower total capital investments (272 million US\$) and bypass (51%). Although total capital investments (305 million US\$) and feed bypass (58%) were higher, the integrated furfural and ethanol biorefinery (Scenario 5) was more economically viable without electricity sales (IRR=10.30%) due to high furfural yield (69%). The economic benefits of furfural and ethanol co-production were limited by the process energy demands, which could only be supplied by feedstock available in the integrated biorefinery.

**Keywords**: furfural, cellulosic ethanol, lignocellulose, sugarcane bagasse, techno economic analysis

\*Corresponding author. Tel.: +27 21 808 9485; fax: +27 21 808 2059. E-mail address: sfarzad@sun.ac.za

#### 1 Introduction

Interest in the production of platform chemicals from biomass resources has increased because of environmental awareness and the necessity of the need to replace fossil resources. The US Department of Energy listed furfural as one of the top platform chemicals, which can be converted to biofuels and biochemicals (Cai et al., 2014). Furfural is almost

exclusively produced from xylose, a monosaccharide that is often found in large quantities in the hemicellulose fraction of lignocellulosic biomass. Industrial production of furfural started in 1921 by Quaker Oats company (Cai et al., 2014; Zeitsch, 2000), but yield and production methods have not improved significantly since 1980s (Cai et al., 2014); improvements to production strategies are therefore required. Co-production of furfural with valuable chemicals or fuels may improve the economic viability of furfural production. Furfural can be produced directly from lignocellulose in a single process unit as it is currently practiced commercially (Cai et al., 2014; Dashtban et al., 2012). In fact, furfural is only produced from the pentosans component of biomass, therefore furfural can be co-produced with cellulosic ethanol in a biorefinery system (Farzad et al., 2017).

Similarly, commercial manufacturing of cellulosic ethanol as one of the preferred biofuel options, is limited by high production costs, partly due to the cost of lignocellulose pretreatment, which negatively affect the overall economics (Cardona et al., 2010; Jin et al., 2019). Commercial "second generation" ethanol plants exist (Jin et al., 2019), but currently contribute less than one percent to annual ethanol production globally (Cardona et al., 2010; Jin et al., 2019). The recalcitrant nature of lignocellulosic material necessitate the use of energy intensive pretreatment processes that make the cellulose susceptible to enzymatic hydrolysis, and have been one of the primary reasons for delayed commercialization of second generation ethanol production tend to convert the hemicellulosic component of lignocellulosic material to pentose sugars that can be potentially converted to a high value biochemical such as furfural (Cai et al., 2014; Cardona et al., 2010). The use of furfural residues for ethanol co-production provides an opportunity to improve the economic viability of

commercial production of cellulosic ethanol, due to associated furfural revenue (2200 US\$/tonne) (Giuliano et al., 2018; Rosales-Calderon and Arantes, 2019; Yan et al., 2014).

Similar to pretreatment required for ethanol production, the industrial furfural process is associated with high steam demand, both for conversion of pentosans to furfural and stripping off furfural in the vapor phase (Silva et al., 2017; Zeitsch, 2000). Furfural production is generally conducted in the temperature range of 170-200°C under autohydrolysis or with additional acidic catalyst such as sulphuric acid (Cai et al., 2014; Dashtban et al., 2012; Zeitsch, 2000); similar to temperatures for steam pretreatment for ethanol production (Avci et al., 2013; Cardona et al., 2010). Both the industrial furfural process and ethanol pretreatment are energy intensive and costly.

Commercial furfural production plants that utilize sugarcane bagasse as feedstock are generally annexed to a sugar mill, where the process energy demands are met by burning the lignocellulosic residues supplemented by coal (Smithers, 2014). Although the furfural process can serve as pretreatment required for ethanol production, the addition of ethanol production to the furfural process will increase overall energy demands considering the need for ethanol recovery and purification to meet market product specifications (Silva et al., 2017). Implementation of energy self-sufficient biorefinery concept helps avoid the use of coal and this is achieved by bypassing a fraction of the lignocellulosic feedstock directly to the boiler, to substitute the fossil fuel (Farzad et al., 2017; Mandegari et al., 2017a). Therefore, meeting the energy demands of process scenarios considered in the present project in a self-sufficient manner will lower the amount of biomass available for conversion to ethanol and/or furfural.

Economic assessment of furfural and ethanol co-production from lignocellulosic material has been studied previously, typically by first producing a xylose-rich hydrolysate, from which furfural is subsequently produced, while the solid residues are converted to ethanol through separate hydrolysis and fermentation (SHF) (Farzad et al., 2017; Giuliano et al., 2018; Moncada et al., 2016; Zhao and Liu, 2019). These previous studies show that employing the two-stage furfural process favours the integration of furfural and ethanol production when organic solvents are employed for furfural purification and recovery. Moreover, these studies previous studies also show that pretreated biomass require washing to remove yeast inhibitors prior to fermentation. However, the use of organic solvents and washing of pretreated biomass negatively affects the environment and increases process (operating and capital) costs (Farzad et al., 2017; Mokomele et al., 2018). Alternatively, the one-stage furfural process is well configured to minimise capital costs, as it requires less reactors compared to the two-stage furfural process and the use of inhibitor resistant yeast eliminates the need for washing pretreated biomass.

There is lack of techno-economic evaluation studies focused on the one-stage furfural production at different conditions production, followed by ethanol co-production from furfural solid residues using the simultaneous saccharification and fermentation (SSF) technique without detoxification prior. Moreover, techno-economic studies evaluating integrated one-stage furfural and ethanol co-production in an energy self-sufficient biorefinery system can be insightful for bioeconomy development. The aim of the present study is to provide a techno-economic comparison of one-stage furfural production integrated with ethanol co-production of furfural-only and ethanol-only production from lignocellulosic biomass (sugarcane bagasse and harvest residues). Mass and energy balances were generated using Aspen Plus® process simulation, and used to determine capital and

operating costs of the various biorefinery scenarios. Costing data was used to determine the minimum ethanol selling prices (MESP) and internal rates of return (IRRs), using the discount cash flow method.

### 2 Process simulation and economic evaluation methodology

In this study, one-stage furfural production from mixture of sugarcane bagasse and harvest residues integrated with SSF ethanol production from the furfural residue at different conditions (described in Section 2.1) was simulated in Aspen Plus® V8.8 (Aspen Technology Inc., USA). Mass balance data i.e., fractional conversions at various conditions, obtained in previous studies (Ntimbani et al., 2021) from furfural and ethanol experiments were applied in simulation of furfural and SSF reactors of the developed models. Ethanol only scenario served as the base case from which MESP and energy demands were evaluated without furfural co-production. Furfural only scenario was also developed to allow comparison with integrated furfural and ethanol scenarios as well as the sole ethanol scenario. Thereafter, the internal rate of return (IRR) from all the biorefinery scenarios were calculated using the market prices of products to determine profitability (Farzad et al., 2017).

The simulation models were developed based on the Electrolyte non-random two-liquid (ELECNTRL) thermodynamic model found in Aspen Plus<sup>®</sup> properties database as it is suitable for modelling mixtures with non-ideal behavior and partially immiscible systems (Gebreyohannes et al., 2014; Mandegari et al., 2017a). The simulation models (described in section 2.1) include distillation units for purification of the furfural and ethanol to evaluate the required energy to meet the market product specifications for the respective products.

It was noted from literature that certain biorefinery compounds and their properties are not available on Aspen Plus<sup>®</sup> databases (Mandegari et al., 2017a; Moncada et al., 2016). Thus, properties of these components were either calculated where possible or estimated and the known properties such as molecular weights were inserted and then exported into the properties module.

As in previous studies (Kapanji et al., 2019; Mandegari et al., 2017a; Özüdoğru et al., 2019), a mixture of sugarcane bagasse (70 wt.%) and harvest residues (30 wt.%) with final feedstock mass composition of 40.7% cellulose, 27.1% hemicellulose, 21.9 % lignin, 6.75% extractives and 3.5% ash with 50% moisture content was used as biomass feedstock in simulation studies (Kapanji et al., 2019; Özüdoğru et al., 2019). The mixture of bagasse and harvest residues was assumed to exhibit same properties as bagasse, thus, experimental data based on bagasse (Ntimbani et al., 2021) were assumed to be applicable to the feedstock mixture of bagasse and harvest residues. Harvest residues are the brown leaves usually burned in cane fields and were included in this study to have a capacity that is consistent with previous studies and feedstock availability in South Africa (Mandegari et al., 2017a). The biorefinery was developed considering dry biomass availability of 65 tonne/hr (45 tonne/hr bagasse and 20 tonne/hr harvest residues) based on data from typical South African sugar mills (Farzad et al., 2017; Mandegari et al., 2017a).

#### 2.1 Scenario Description

An energy self-sufficient furfural only (scenario 1) shown in Figure 1a was developed using the Rosenlew industrial furfural process and yield data (Silva et al., 2017; Zeitsch, 2000), in order to compare the commercial furfural process with the integrated furfural and ethanol

biorefinery scenarios. Sole ethanol (scenario 2) production (Figure 1b), which served as base case, employed steam explosion as lignocellulose pretreatment at 205°C followed by SSF of the whole slurry employing CelluX™4 as yeast, using data from previous works (Mokomele et al., 2018). The ethanol only scenario was developed to allow energy demands and MESP comparison of ethanol production without furfural and furfural with ethanol co-production scenarios.

Different scenarios investigating furfural and ethanol co-production from sugarcane lignocelluloses in an energy self-sufficient biorefinery via one-stage method for furfural production and SSF technique for ethanol production from furfural residues, were developed and evaluated in this study. Based on experimental data in previous reports (Ntimbani et al., 2021), temperature in the range of 170-185°C with and without sulphuric acid was implemented for development of different scenarios. Scenarios 3, 4 and 6 investigated autocatalytic furfural production at 170°C, 200°C and 185°C, respectively (Ntimbani et al., 2021). Whereas, scenarios 5 and 7 were focused on catalytic furfural production with 0.5 wt.% H<sub>2</sub>SO<sub>4</sub> addition at 170°C and 185°C, respectively (Ntimbani et al., 2021). The subsequent fermentation process utilized the furfural residues without detoxification of yeast inhibitors and employed an industrial yeast, CelluX<sup>™</sup>4 (Ntimbani et al., 2021). The investigated scenarios varied in operating conditions, yield and consequently size, but the process flow diagram of all furfural and ethanol co-production scenarios remained identical as shown in Figure 1c. Data used for developing scenarios is provided in Table S1 of supplementary file.

It should be noted that all scenarios were developed to be energy self-sufficient, therefore a portion of lignocellulosic feedstock had to be bypassed to boiler for steam and electricity production not only to supply the heat and power demand of biorefinery, but also the

adjacent sugar mill from which the lignocelluloses were obtained (Mandegari et al., 2017a). Consequently, the required bypass of the feedstock to boiler for steam and electricity production varied between scenarios as a function of energy requirements of each scenario, which was calculated following trial and error approach in Aspen. Furfural and ethanol yield data implemented in the furfural and ethanol integrated biorefinery simulations were obtained from previous experimental data (Ntimbani et al., 2021). Pentosans and pentose sugars were simulated as xylan and xylose, respectively (Hossain et al., 2019), while hexosans and the main hexose sugars were simulated as cellulose and glucose available in Aspen Plus<sup>®</sup> databank, respectively (Hossain et al., 2019). Degradation products leading to pseudo-lignin from pretreatment/furfural production were modelled as tar (Humbird et al., 2011), which is available in Aspen Plus<sup>®</sup> databank.



Figure 1: a) Furfural only biorefinery scenario process flow diagram (PFD), b) Ethanol only biorefinery scenario PFD, and c) Furfural and ethanol co-production biorefinery scenarios PFD including boiler as well as power and steam generation

#### 2.2 Process flowsheet development

#### 2.2.1 Furfural production, recovery and purification

The Rosenlew furfural reactor (180°C and 90 min residence time) used industrially was selected for the sole furfural production (scenario 1) where steam contacts with biomass in a countercurrent manner with furfural vapor product being released continuously from the top (Silva et al., 2017; Zeitsch, 2000), as demonstrated in the block flow diagram (Figure 2). The feedstock in scenarios 3-7 is sent to the furfural steam jacket reactor(s) where it is mixed with water to make up 20 wt.% solids and continuously heated to target temperature for 90 minutes as per laboratory experiments. The principle of the proposed steam jacketed furfural reactor is similar to the Multi-Turbine-Column furfural reactor (de Jong and Marcotullio, 2010), continuously stirs biomass slurry and releases furfural vapor product (Figure 2).

The produced furfural is continuously released at the top of the reactor as vapor and sent for purification and recovery by distillation train comprised of three columns, whereby the first column removes water at the bottom outlet and the volatile organic compounds such as formic acid and methanol are removed at the top (Nhien et al., 2016; Silva et al., 2017; Zeitsch, 2000). The bottom product from the first column is sent for water treatment. The top product of the first column is sent to a second column where the furfural in the stream is recovered as bottom product and the top product contains the volatile organic compounds (Nhien et al., 2016; Silva et al., 2017; Zeitsch, 2000). A side product from the first column is withdrawn and sent to the second column where it is further purified and recovered as the bottoms product, which is sent to a decanter; this has heavy phase rich in furfural and light phase containing water and acetic acid as well as some furfural (Nhien et al., 2016; Silva et al., 2017). The heavy phase of the decanter containing furfural is sent to the third column where it is purified to

>99.5 wt.% and recovered (Nhien et al., 2016; Silva et al., 2017; Zeitsch, 2000). The light phase is sent back to the first column with the aim of recovering the remaining furfural (Nhien et al., 2016; Silva et al., 2017).



Figure 2: Block Flow Diagram in the form of Aspen Plus<sup>®</sup> screen shot of steam explosion; furfural production, purification and recovery; Simultaneous Saccharification and fermentation

## 2.2.2 Steam explosion pretreatment

Steam explosion (Figure 2) was selected as the pretreatment method for the ethanol only production scenario because it has a higher energy efficiency and result in lower environmental impact (Mandegari et al., 2017a) as well as availability of data obtained using sugarcane bagasse and harvest residues (Mokomele et al., 2018). Additionally, steam explosion has been found to make biomass susceptible to enzymatic hydrolysis required for the production of fermentable sugars, and allows that the whole pretreatment-slurry be sent for ethanol production (Mokomele et al., 2018).

### 2.2.3 Bioethanol production

Ethanol production (Figure 2) was carried out using furfural residues in scenarios that evaluated furfural and ethanol co-production, while whole-slurry obtained from steam explosion was used as feedstock in ethanol only biorefinery (Scenario 2). The solid residues from the furfural process or steam explosion whole-slurry were cooled to 37°C prior to being fed into the bioreactors. The bioreactors were operated at 10% solids for 120 hours at 37°C and stirring speed of 150 rpm with addition of purchased enzymes (26 mg protein/g dry solids, 19 Cellic CTec2<sup>\*</sup> and 7 mg Cellic HTec2<sup>\*</sup>) and yeast culture of CelluX<sup>TM</sup>4 as well as corn steep liquor and diammonium phosphate. The SSF bioreactors were operated for 120 hours at 37°C and stirring speed of 150 rpm. The resulting fermentation broth was sent to the ethanol purification and recovery unit after the duration of the SSF process (Humbird et al., 2011).

#### 2.2.4 Bioethanol purification and recovery

Fuel grade ethanol was recovered from the purification and recovery section, which primarily separates anhydrous ethanol, water, and combustible solids from fermentation broth using distillation (Humbird et al., 2011; Mandegari et al., 2017a). Ethanol purification employed a set of columns namely the beer column in which strongly non-ideal liquid was selected as the convergence method and the rectification column in which the standard method was selected and operated as described in previous studies (Farzad et al., 2017; Mandegari et al., 2017a). The property package for this section was NRTL-HOC (Humbird et al., 2011; Mandegari et al., 2017a). Similar to previous studies, adsorption with molecular sieve was selected for the production of ≥99.50 wt% ethanol (Farzad et al., 2017; Humbird et al., 2011; Mandegari et al., 2017b). The wet insoluble solids and the stillage water were sent to the evaporation unit.

## 2.2.5 Evaporation unit

The evaporation unit removed moisture from the wet insoluble solids from the purification and recovery unit, to produce a syrup that was sent for combustion, as this is believed to outweigh wastewater treatment costs (Farzad et al., 2017; Mandegari et al., 2017a). The furfural only Scenario 1 did not have the evaporation unit because the furfural residues contained moisture of about 40-50%, which is similar to bagasse from the sugar mill and were sent directly to the boiler unit as supplement fuel. A flash drum and a pneumatic pressure filter were used to separate the wet solids and the liquid was concentrated in a multiple effect evaporator to produce a syrup with some of the liquid utilised as process water (Farzad et al., 2017; Mandegari et al., 2017a).

#### 2.2.6 Wastewater treatment (WWT) unit

Wastewater produced from either the furfural production or ethanol production or both was treated in the WWT unit prior to being reused in the biorefinery or release into the environment (Farzad et al., 2017; Humbird et al., 2011). Similar to previous studies, the resulting treated water from the WWT unit was assumed to be reusable by the biorefinery/sugar mill, thereby reducing amount of fresh make-up water needed (Mandegari et al., 2017a). The configuration of the WWT unit adapted for this study can be found in previous publications (Mandegari et al., 2017a).

#### 2.2.7 Combined heat and power (CHP) unit

The CHP plant (combustor, boiler and turbo generator subsystem) was used to generate steam and electricity required by the biorefinery and sugar mill. Feedstock bypassed and any unconverted biomass from biorefinery as well as the various organic by-products from processes were burned as fuel. Condensing-extraction steam turbines (CEST) were designed

to allow extraction of steam at different conditions (low and high pressure) to provide for energy demands by the biorefinery and sugar mill (Mandegari et al., 2017a). The CEST produced electricity as a by-product from power output corresponding to steam extracted. Surplus electricity (AC) from the CEST provided a co-product credit and was assumed to be sold to the grid (Farzad et al., 2017; Kapanji et al., 2019; Mandegari et al., 2017a).

#### 2.3 Economic evaluation

Simulations provided all the essential technical inputs for the subsequent assessment of the economic performance of alternative scenarios, to ultimately identify the most desirable biorefinery scenario. The economic assessment of investigated scenarios was carried out using the Aspen Plus<sup>®</sup> Economic Evaluator and literature data, to estimate the purchased and installed cost of equipment, as well as the variable and fixed operating costs (Humbird et al., 2011; Moncada et al., 2016). It was noted from literature that Aspen Economic Analyser cost estimations of certain equipment namely the boilers, turbo-expanders, generators, reactors, waste water treatment basins are not precise (Farzad et al., 2017; Humbird et al., 2011). Therefore, technical data was applied to provide better estimates of such process units (Humbird et al., 2011; Mandegari et al., 2017a).

The variable cost included cost of feedstock and process reagents as well as costs associated with disposal of waste. On the other hand, fixed costs included labour, plant maintenance and property insurance. Additional economic parameters to account for, is tax rate in South Africa. To compute purchased cost and installed cost of the equipment from published data, the cost estimation formulas were used accordingly coupled with the respective installation factors and scaling exponents (Humbird et al., 2011). To account for depreciation over plant life, the

straight line depreciation method was assumed (Mandegari et al., 2017a; Moncada et al., 2016).

The internal rate of return (IRR) of each scenario was computed using market prices of products given in Table 1 to evaluate profitability of each scenario (Farzad et al., 2017; Mandegari et al., 2017a). Minimum ethanol selling price (MESP) were also evaluated in all ethanol producing scenarios at various discount rates or IRRs (10, 15, 20%) to determine which scenario has the most potential to lower ethanol selling price (Petersen et al., 2014). Sensitivity analysis evaluating effects of FCI, production costs, furfural and ethanol selling price, electricity price and income tax on IRR was conducted. The applied parameters/methods for economic evaluation are reported in Table 1.

Parameters	Value
Annual operating hours	6480 h
Project life	25 years
Finance	100% equity
Discount rate	9.7% for real term DCF analysis
Income tax rate	28%
Depreciation	Straight line over 5 years (20% per year)
Salvage value	0
Construction period	2 years
% Spend in year -2	10%
% Spend in year -1	60%
% Spend in year 0	30%
Working capital	5% of fixed capital investment
Start-up time	2 years
First year production capacity	50%
Second year production capacity	75%
Electricity selling price	0.08 US\$/kWh
Furfural price <sup>1</sup>	2200 US\$/tonne
Ethanol price <sup>2</sup>	0.596 US\$/L
Enzymes cost <sup>3</sup>	1000 US\$/tonne
Cost year for analysis	2018

Table 5: Economic analysis parameters adapted from previous works (Kapanji et al., 2019; Özüdoğru et al., 2019).

(<sup>2</sup>Farzad et al., 2017; <sup>3</sup>Gubicza et al., 2016; <sup>1</sup>Rosales-Calderon and Arantes, 2019; Yan et al., 2014)

### **3** Results and discussions

#### 3.1 Mass and energy balances

The overall mass and energy balances (heating, cooling and power demand) of the simulated biorefinery scenarios are presented in Table 2, which includes the required bypass of the feedstock to the CHP units, according to the energy demands/balances of the various scenarios. Ethanol-furfural co-producing scenarios required 49-60% feedstock bypass to boiler which is higher compared to sole production of ethanol (Scenario 2) that needed 40% bypass where steam explosion was employed as pretreatment. The steam consumption per kg of feedstock in steam explosion pretreatment (0.21 kg steam per kg biomass) is less than the steam consumed by the furfural reactors in Scenarios 3-7 (0.42-0.64 kg steam per kg biomass) as shown in Table 2. Previous studies with the same feedstock availability found that 58% bypass was required for furfural and ethanol co-production (Farzad et al., 2017), which is within the 49-60% bypass found in furfural and ethanol coproduction scenarios of this study. The furfural only biorefinery (Scenario 1) required 51% bypass primarily due to the steam to biomass ratio (1.7 kg steam per kg of biomass with ~50% moisture) requirements of the Rosenlew furfural reactor (Silva et al., 2017; Zeitsch, 2000). The steam requirements in the Rosenlew reactor enables furfural recovery as vapor with minimal degradation while limiting absorption by residual biomass flowing down the reactor (Silva et al., 2017; Zeitsch, 2000). Employing a 20% solids steam jacket vapor releasing reactor for furfural production as per previous experiments (Ntimbani et al., 2021) reduced the steam requirements of furfural reactor by two to five folds depending on reactor operating temperature, thereby, allowing furfural and ethanol integration with 49-60% bypass requirements.

Formation of pseudo-lignin at more severe conditions of furfural production reduced the required bypass, since it was recovered and utilised as supplement fuel to the boiler. Pseudo-lignin formation was more prevalent in scenario 7 (CSF=3.58) as indicated by previous experimental results (Ntimbani et al., 2021) and increased the amount of material used as boiler fuel. According to simulation results (Table 2), the total steam produced by the boiler in scenario 7 (311 tonne/hr), exceeded the total steam produced in scenarios 3-6 (280-294 tonne/hr) although the bypass was 49% in Scenario 7 compared to 58-60% found in furfural and ethanol co-production Scenarios 3-6. Pseudo-lignin formation is generally increased by higher process severity conditions where pentosans and hexosans are degraded to form solids that have properties similar to lignin and releases energy when combusted (Hu et al., 2012). Heating demands of sole furfural (1074 kW/ton of feed) and sole ethanol production (698 kW/ton of feed) scenarios reported in Figure 3, determined per mass of biorefinery feedstock.

kW/ton of feed) scenarios reported in Figure 3, determined per mass of biorefinery feedstock, were more than doubled when furfural and ethanol production were integrated into a single biorefinery (1870-2133 kW/ton of feed). Integrating furfural and ethanol production (scenarios 3-7) necessitated replacement of steam explosion pretreatment by the one-stage furfural process (scenario 1), which required overall heating demands that were 45% more than the sole ethanol production (scenario 2). The high heating duties associated with the one-stage furfural process were attributed to the steam needed to continuously release furfural vapor product (Scenario 1) or maintain 20% biomass slurry furfural reactor at target temperature (Scenario 3-7) to minimize furfural degradation (Nhien et al., 2016; Silva et al., 2017). The combined heating duties for ethanol and furfural purification and recovery in Scenarios 3-7 also contributed towards the increase of the overall heating duties in comparison to sole ethanol (Scenario 1) and furfural production (Scenario 1). Although the furfural process is characterised with high temperature streams, not all of the available heat

could be recovered for heating elsewhere, due to thermodynamic limitations (Nhien et al., 2016).

The increase of heating energy demands (supplied by bypassing a portion of feedstock to boiler) negatively affected the overall productivity of furfural in furfural and ethanol integrated biorefineries. Although furfural yield was 68.73% (Ntimbani et al., 2021) in scenario 5, higher overall production of furfural was achieved in scenario 1 (3804 kg/hr) where the yield was 59.9% (Zeitsch, 2000) instead of scenario 5 (3754 kg/hr) where furfural yield was 10% higher (Table 2). Bypass requirements of Scenario 1 and 5 were 51 and 58%, respectively, showing that higher heating demands of scenario 5 limited the feedstock available for the biorefinery and resulted in lower overall furfural production regardless of higher furfural yield. The overall furfural productivity in scenario 7 (3454 kg/hr) was not sufficient to surpass the furfural production in Scenario 1 (3804 kg/hr) due to the associated lower furfural yield of 50.47% (Ntimbani et al., 2021) compared to 59.90% in Scenario 1, irrespective of the two percent bypass difference between Scenario 1 (51%) and Scenario 7 (49%).

The overall ethanol production was reflected by ethanol yield based on hexosans and pentosans content of feed to the ethanol production stage rather than ethanol yield based on released monomeric sugars primarily produced by enzymatic hydrolysis. For instance, ethanol yields based on released monomeric sugars in Scenarios 5 and 6 reported as 95.80 and 88.84%, respectively (Ntimbani et al., 2021) were misleading since the corresponding ethanol production rates of Scenarios 5 and 6 were 2452 and 5167 kg/hr, respectively (Table 2). Ethanol production complexities caused by involved factors such as solids digestibility, cellulose degradation during furfural production as well as yeast inhibition, make the theoretical yield based on released sugars less reliable in reflecting overall ethanol production

in the integrated one-stage furfural and ethanol biorefineries. Ethanol yield based on initial hexosans and pentosans content of feed to the ethanol production stage gave a reliable reflection of the expected overall ethanol production rate i.e., ethanol yield based on initial hexosans and pentosans content in Scenarios 5 and 6 were 55 and 78% with corresponding ethanol production of 2452 and 5167 kg/hr (Table 2).

	Unit	Scenario						
	onit	1	2	3	4	5	6	7
Feedstock								
Bypass to boiler	t/hr	59.04	44.28	68.12	68.12	65.85	68.12	55.63
	%	51.00	40	60.00	60.00	58.00	60.00	49.00
To biorefinery	t/h	54.49	69.25	45.41	45.41	47.68	45.41	57.90
Products								
Ethanol yield								
(based on initial	%	-	95.69	63.79	74.71	53.51	77.30	17.02
glucan & xylan) <sup>1</sup>								
Ethanol	kg/h	0	11184	4203	4108	2452	5167	1650
Furfural yield <sup>2</sup>	%	59.50	-	13.68	31.14	68.73	29.00	50.47
Furfural	kg/h	3804		690	1527	3754	1560	3454
Surplus	N // N /	22.22	14 57	22.07	20.97	21.62	20.22	22.66
electricity		25.57	14.57	22.07	20.87	21.05	20.25	25.00
Energy demands								
Cooling	MW	53.24	52.08	40.22	42.86	41.37	35.70	35.99
Heating	MW	58.54	48.32	96.86	94.57	96.99	90.49	108.26
Power	MW	1.20	1.63	1.77	1.72	1.70	1.72	1.75
F Furfural reactor								
or pretreatment	kg/kg	1.67	0.21	0.42	0.63	0.62	0.51	0.64
steam/Feed								
LPS/FF	kg/kg	24.87	-	97.90	39.90	18.01	35.69	20.28
HPS/FF	kg/kg	23.92	-	27.68	18.65	7.84	14.93	10.73
LPS/EtOH	kg/kg	-	6.89	10.53	9.73	13.60	7.78	21.01
Total Steam @	(tonne	200	222	20/	283	201	280	211
452°C & 62atm*	/hr)	309	222	294	205	291	280	511

Table 6: Overall mass and energy balance of the studied biorefinery scenarios

<sup>1</sup>Ethanol yield calculated based on initial xylan and glucan feed to ethanol production from previous works (Ntimbani et al., Unpublished Results; Mokomele et al., Unpublished Results); <sup>2</sup>furfural yield of Scenario 1 is from literature (Zeitsch, 2000) and the rest as found in previous works (Ntimbani et al., Unpublished Results); \* Total steam produced (kg/hr) by the boiler at 452°C & 62 atm using feed bypass and supplement fuel produced as waste by the biorefinery.



Figure 3: Heating, cooling and power duties per ton of feedstock investigated biorefinery scenarios

# **3.2** Economic analyses

The economic analyses implied that furfural biorefinery (scenario 1) required the least capital investments (272 million US\$) compared to sole ethanol biorefinery (scenario 2) and the integrated furfural and ethanol biorefineries (scenario 3-7) that required capital investments of 294 million US\$ and 305-327 million US\$, respectively (Table 3). The need for evaporation section to reduce moisture of solids from enzymatic hydrolysis and fermentation section prior to being sent to the boiler as supplement fuel and the need for molecular absorption sieves in ethanol purification, contributed towards higher capital costs in scenario 2 when compared to scenario 1. The solids from furfural production in scenario 1 contained 50% moisture and were sent directly to the boiler as described in literature (Silva et al., 2017; Zeitsch, 2000). The combined furfural and ethanol production and recovery sections in addition to the

evaporation section in furfural and ethanol integrated biorefineries (scenarios 3-7) resulted in the integrated biorefinery scenarios having the greatest need for capital investments.

The profitability of ethanol production was improved when co-produced with furfural as evidenced by IRR of 12.78% (scenario 5) in comparison to IRR of 10.18% found in scenario 2, where sole ethanol production was performed (Table 3). The IRR of other furfural and ethanol co-producing scenarios (3, 4, 6, 7) was in the range of 7.19-10.54% and were not economically worthwhile since the corresponding IRRs were either below IRR (10.18%) found in sole ethanol production (scenario 2) or resulted in IRR (10.54% in scenario 7) closer to IRR value in sole ethanol production. The profitability of Scenario 5 was mainly boosted by furfural yield (68.73%), which was higher compared to 14-50% yields in the rest of the furfural ethanol integrated biorefineries (scenario 3, 4, 6, 7). Amongst the furfural and ethanol integrated scenarios, scenario 5 had one of the lowest TCI (305 million US\$) and the fact that total costs of production (TCOP) of the furfural and ethanol integrated scenarios similar (18.12-18.89 million US\$/year), rendered scenario 5 most profitable furfural and ethanol biorefinery.

Although furfural co-production improves the profitability of ethanol production, ethanol coproduction does not benefit the economic viability of furfural production, in the context of an integrated, multi-product biorefinery. There was a decrease of IRR (12.92%) in sole furfural production (scenario 1) when ethanol co-production was introduced as the IRR (3.64-12.78%) in scenarios 3-7 were below 12.92% (Table 3). Furfural only biorefinery had the lowest TCI (272 million US\$) and TCOP (13.70 million US\$/year) since there were no evaporation and ethanol production sections. Moreover, furfural yield of 59.90% and bypass of 51% in Scenario 1 resulted in higher furfural production flow rates (3804 kg/hr) compared to scenario

5 (3754 kg/hr), which had a higher furfural yield (68.73%), but suffered from higher bypass due to energy requirements.

Without electricity sales, furfural and ethanol coproduction in scenario 5 results in a higher IRR (10.30%) compared to IRR of 9.91% and 8.26% in biorefineries focused on only furfural (scenario 1) or ethanol (scenario 2) production (Table 3). The absence of electricity credit reduced IRR (12.92%) of scenario 1 by three percent to 9.91%, while IRR (12.78%) of scenario 5 reduced by 2.48% to 10.30%. Therefore, profitability of scenario 5 is less dependent on electricity sales in comparison to scenario 1 due to higher furfural yield (68.73%) in scenario 5 compared to yield in scenario 1 (59.9%). Moreover, ethanol produced in scenario 5 also reduces dependency of profitability on electricity sales. The absence of electricity sales caused the least decrease of IRR (10.18%) in scenario 2 which decreased by 1.92% to 8.26%. The high yield (95%) of ethanol in scenario 2 resulted in profitability being dominated by ethanol sales. Noting that scenario 2 had the lowest bypass (40%) indicating lower steam requirements in comparison to other scenarios (51-60%), while considering that the CHP plant was designed based on steam demands and minimal electricity production as a coproduct corresponding to work done by CEST during extraction of required steam (Mandegari et al., 2017), electricity sales were less dominant in scenario 2.

Avoiding the use of organic solvents for furfural separation allowed ethanol co-production integrated with the one-stage furfural to compete economically against the ethanol production integrated with the two-stage furfural process utilising organic solvents. Under the same economic parameters, as shown in Table 3, the IRR of scenario 5 (best case) was higher (8.09%) than 7.50% found in previous studies (Farzad et al., 2017) in two-stage furfural and ethanol biorefinery utilising tetrahydrofuran for furfural separation. The high purchase

and recovery costs of solvents negatively affected the IRR of ethanol production integrated with the two-stage furfural process and caused environmental burdens as revealed by previous works (Farzad et al., 2017). It is noteworthy that employing inhibitor-resistant yeast enabled integration of one-stage furfural process with ethanol production, otherwise, deriving ethanol from furfural residual solids would not be economically competitive due to low ethanol yields (Cardona et al., 2010; Jin et al., 2019).

Table 7: Key economic results for investigated furfural and ethanol biorefineries from lignocellulose at 2018 cost year of analysis

	TCI (million US\$)	TCOP (million US\$/year)	Furfural yield (%)	Ethanol yield (%)	IRR (%)	IRR (%) without electricity credit
Scenario 1	272	13.70	59.50	-	12.92	9.91
Scenario 2	294	18.12	-	95.69	10.18	8.26
Scenario 3	327	18.37	13.68	63.79	3.64	-0.56
Scenario 4	306	18.17	31.14	74.71	7.19	3.99
Scenario 5	305	18.57	68.73	53.51	12.78	10.30
Scenario 6	305	18.17	29.00	77.30	8.64	5.80
Scenario 7	322	18.89	50.47	17.02	10.54	7.69
Scenario 5* (2015 cost year)	264	17.03	68.73	53.51	8.09	4.90

Furfural yield is based on pentosan content of feed to furfural reactor; Ethanol yield % is based on initial hexosan & pentosan of feed to biorefinery; Furfural price=2200 US\$/tonne (Rosales-Calderon and Arantes, 2019); Ethanol price=0.595 US\$/L (Farzad et al., 2017); TCI is total cost of investment; TCOP is total cost of production. \*Economic calculations based on 2015 cost year analysis using same parameters as in previous works (Farzad et al., 2017)

Integrated furfural and ethanol scenarios 5 and 7 were able to achieve MESPs (-0.02 and 0.42 US\$/L) that were lower than the MESP (0.595 US\$/L) at scenario 2 (sole ethanol) when the target discount rate (IRR) was 10% (Table 4). A negative MESP in scenario 5 indicates that the discount rate of 10% could be reached without ethanol sales regardless of capital and operational costs associated ethanol production. However, the capital investment

requirement (305-327 million US\$) in furfural and ethanol integrated biorefineries (scenario 3-7) resulted in MESPs (1.14-2.23 US\$/L) that were at least 37% higher than the MESP (0.83 US\$/L) required in ethanol only biorefinery when the target IRR is 15% or more. The MESPs of furfural and ethanol integrated biorefinery scenario 5 and 7 were also negatively affected by lower ethanol yields of 53% and 17%. The high ethanol yields (95%) and lower fixed capital investment (294 million US\$) in scenario 2 results in MESPs (0.83 US\$/L) that are lower when compared to MESPs (1.14-2.23 US\$/L) in integrated furfural and ethanol integrated biorefineries at 15% IRR.

Table 4: Minimum ethanol selling price (MESP) at various discount rates (IRR) for all the ethanol producing biorefinery scenarios with and without electricity credit

Discount rate % (IRR)	10	15	20			
	MESP (US\$/L) with electricity credit					
Scenario 2	0.59	0.83	1.13			
Scenario 3	1.28	1.98	2.84			
Scenario 4	0.92	1.61	2.46			
Scenario 5	-0.02	1.14	2.54			
Scenario 6	0.73	1.27	1.94			
Scenario 7	0.42	2.23	4.43			

The amount of feedstock to the biorefinery was increased to evaluate the effect of scale on MESP by considering scenarios where a sugarmill that has 25% more capacity (375 tonne/hr sugarcane processing) with only purchase of harvest residues corresponding to sugarcane brought to the mill. The 25% increase in scale was selected to ensure that overall furfural production rate does not exceed the 10% annual capacity of 270-300 ktonne (Rosales-
Calderon and Arantes, 2019). Furfural and ethanol integrated biorefinery (scenario 5) benefits from increase in production scale as shown by lower MESPs of -0.29 and 0.70 US\$/L compared to 0.56 and 0.80 US\$/L in scenario 2 at IRR values of 10 and 15%, respectively, when sugarmill with 25% more capacity is considered (Figure 4). However, the higher capital requirements in scenario 5 resulted in MESP (1.98 US\$/L) that is higher than the MESP (1.10 US\$/L) in scenario 2 when target IRR is 20%. The higher MESP in scenario 5 at 20% IRR is also due to lower ethanol yield (53%) in comparison to 95% in scenario 2. In addition to ethanol yield, the scale-up results reveal that the high feed bypass (58%) due to energy demands in scenario 5 compared to scenario 2 (40%) negatively affected the MESP as less feedstock was available to the biorefinery.



Figure 4: Effect of production scale on minimum ethanol selling price (MESP) at various discount rates (IRR).

#### **3.3 Economic sensitivity analysis**

Economic sensitivity analysis was conducted by evaluating the changes in IRR values of all the biorefinery scenarios when income tax, TCOP, FCI, ethanol, furfural and electricity selling prices were increased or decreased by 25%. As shown in Figure 5, all the biorefinery scenarios were more sensitive to a 25% decrease of FCI as the base IRR (12.92, 10.18, 3.64, 7.19, 12.78, 8.64, 10.54%) values increased by larger margins to give higher IRR values (16.7, 13.5, 5.96, 10.05, 16.53, 11.73, 13.94%). Furfural and ethanol production processes are capital intensive due to the cost of furfural reactor and pretreatment reactor combined with the purification and recovery equipment needed to meet market product specifications. The high energy demands also increase the capital expenses associated with the boiler, while also reducing feedstock available to the biorefinery and consequently lowering net revenue from product sales needed to recover capital expenses with higher returns. The FCI of the furfural process can be potentially lowered when the furfural distillation is intensified by combining the two conventional columns into a single thermally coupled column in the form of bottom dividing wall column-decanter as described in other studies (Nhien et al., 2016). In addition, intensifying the furfural distillation train lowers reboiler duty and annual operational costs by 7.9 and 7.3%, respectively (Nhien et al., 2016).

The multi-product biorefinery strategy decreased the economic risk associated with changes in product (ethanol and furfural) prices when compared to biorefinery scenarios focussed solely on either ethanol or furfural production. The variations in IRR of the sole ethanol production (scenario 2) due to ethanol price fluctuations was decreased from 3.41% to 1.68% at most when furfural and ethanol were co-produced in scenarios 3-7 (Figure 5). Likewise, IRR variations due to furfural price fluctuations of the sole furfural production (scenario 1) were decreased from 3.20% to 2.83% at most when furfural and ethanol were co-produced in

scenarios 3-7 (Figure 5). Introduction of either furfural or ethanol to biorefineries focussed only on furfural or ethanol production dilutes contribution of a single product towards the net revenue, thereby, reducing sensitivity.

Since ethanol was derived from furfural residues, the intrinsic determinant of IRR sensitivity to product price is primarily dependent on furfural process conditions that determine fractional conversions of feedstock to desired products and energy requirements as well as overall productivity. Scenario 4 and 6 had a balanced risk exposure to ethanol and furfural price fluctuations as indicated by either a 1.42-1.62% decrease or increase in IRR when product prices were varied by 25% (Figure 5). Furfural and ethanol yields in Scenario 4 and 6 were 29-31% and 75-77%, respectively, thus, considering the value of furfural (2200 US\$/tonne) and ethanol (0.595 US\$/L), the revenue contributions of ethanol and furfural will be roughly evenly distributed (38-44%) with the rest coming from electricity sales. Therefore, either product price fluctuations have a similar effect on the IRR.

Scenarios 5 and 7 multi-product biorefineries were effective in hedging against ethanol price fluctuations in comparison to sole ethanol production, however, exposure to furfural price fluctuations was less mitigated. The IRR sensitivity to ethanol price in the sole ethanol production (scenario 2) decreased by at least five times when ethanol and furfural production were integrated, as demonstrated by IRR variations of 3.41% in scenario 2 compared to only 0.64% and 0.44% in scenarios 5 and 7 (Figure 5). In contrast, scenario 5 and 7 resulted in fractional improvements of IRR exposure to furfural price as shown by 3.2% IRR variation found in the sole furfural production (scenario 1) in relation to 2.83% (scenario 5) and 2.71% (scenario 7) as shown in Figure 5. Furfural yields in Scenario 5 and 7 were 68.73 and 50.47% and resulted in 61-71% contribution by furfural sales towards the total revenue of scenario 5

and 7, hence, the IRR sensitivity to furfural price was dominant. Scenario 3 was the most effective in reducing exposure to furfural price fluctuation as it furfural yield was only 14% and as such, the associated ethanol yield of 63.79% made the biorefinery IRR more susceptible to ethanol price fluctuations rather than furfural.

Overall, biorefinery in scenario 5 was the most profitable regardless of 25% product (ethanol or furfural) price decrease as indicated by IRR of 9.79% compared to 6.51% and 9.52% in biorefineries focused on either ethanol (Scenario 2) or furfural (Scenario 1) production (Figure 5). The revenues of scenario 1 and 2 primary emanates from furfural or ethanol, as such, IRRs are expected to be significantly affected by fluctuations in product prices. Scenario 2 already has a lower IRR (10.18%) compared to scenario 5 (12.78%) and the fact that ethanol yield in scenario 5 was 53% resulted in favourable economics for scenarios 5 due to less dependency on ethanol.



Figure 5: Minimum ethanol selling price sensitivity analysis in the studied furfural and

ethanol co-production scenarios.

#### 4. Conclusions

Ethanol production benefitted from integration with furfural production when furfural yields were high (68%), but the economics of furfural were negatively affected as the IRR values of integrated biorefinery were lower than the IRR of furfural only biorefinery. Higher yields of products (furfural and ethanol) make the biorefinery profitability less dependent on electricity sales. Without electricity sales, the furfural and ethanol integrated biorefinery associated with high furfural yield (68%) became more profitable as the net revenues were dominated by furfural and ethanol rather than electricity. MESPs in integrated furfural and ethanol were not competitive with MESPs in sole ethanol biorefinery above 10% discount rates. However, increasing production scale through consideration of sugarmill with 25% more capacity resulted in competitive MESPs furfural and ethanol integrated biorefinery compared to ethanol only biorefinery at 10 and 15% discount rates. Fixed capital investment have the largest potential to increase IRR of all the scenarios followed by product prices as indicated by sensitivity analysis. Further studies evaluating an alternative furfural process with potential to maximise ethanol when co-produced with furfural are required to explore whether the profitability of furfural and ethanol coproduction can be improved and whether MESP can be lowered.

#### Acknowledgment

We thank National Research Fund (South Africa) and Sugar Milling Research Institute for support. The Sugarcane Technology Enabling Programme for Bioenergy (STEP-Bio), a public: a private partnership between the South African sugarcane processing industry and the Department of Science and Technology (DST) Sector Innovation Fund (SIF) is acknowledged

for partial support. The authors gratefully acknowledge Aspen Technology Inc. for provision of the Aspen Plus<sup>®</sup> academic licenses used to carry out this work, Aspen Plus<sup>®</sup> is a registered trademark of Aspen Technology Inc.

#### References

- Avci, A., Saha, B.C., Kennedy, G.J., Cotta, M.A., 2013. High temperature dilute phosphoric acid pretreatment of corn stover for furfural and ethanol production. Ind. Crops Prod. 50, 478–484. https://doi.org/10.1016/j.indcrop.2013.07.055
- Cai, C.M., Zhang, T., Kumar, R., Wyman, C.E., 2014. Integrated furfural production as a renewable fuel and chemical platform from lignocellulosic biomass. J. Chem. Technol. Biotechnol. 89, 2–10. https://doi.org/10.1002/jctb.4168
- Cardona, C.A., Quintero, J.A., Paz, I.C., 2010. Production of bioethanol from sugarcane bagasse: Status and perspectives. Bioresour. Technol. 101, 4754–4766. https://doi.org/10.1016/j.biortech.2009.10.097
- Dashtban, M., Technologies, A., Dashtban, M., 2012. PRODUCTION OF FURFURAL: OVERVIEW AND CHALLENGES. J. Sci. Technol. For. Prod. Process. 2, 44–53.
- de Jong, W., Marcotullio, G., 2010. Overview of Biorefineries based on Co-Production of Furfural, Existing Concepts and Novel Developments. Int. J. Chem. React. Eng. 8, 1–24. https://doi.org/10.2202/1542-6580.2174
- Farzad, S., Mandegari, M.A., Guo, M., Haigh, K., Shah, N., Görgens, J.F., 2017. Multi-product biorefineries from lignocelluloses: A pathway to revitalisation of the Sugar Industry?
  Biotechnol. Biofuels 10, 1–24. https://doi.org/10.1186/s13068-017-0761-9

- Gebreyohannes, S., Neely, B.J., Gasem, K.A.M., 2014. One-parameter modified nonrandom two-liquid (NRTL) activity coefficient model. Fluid Phase Equilib. 379, 196–205. https://doi.org/10.1016/j.fluid.2014.07.027
- Giuliano, A., Barletta, D., Poletto, M., 2018. Techno-economic assessment of a lignocellulosic biorefinery co-producing ethanol and xylitol or furfural. https://doi.org/10.1016/B978-0-444-64235-6.50105-4
- Hossain, S., Theodoropoulos, C., Yousuf, A., 2019. Techno-economic evaluation of heat integrated second generation bioethanol and furfural coproduction. Biochem. Eng. J. 144, 89–103. https://doi.org/10.1016/j.bej.2019.01.017
- Hu, F., Jung, S., Ragauskas, A., 2012. Pseudo-lignin formation and its impact on enzymatic hydrolysis. Bioresour. Technol. 117, 7–12.
   https://doi.org/10.1016/j.biortech.2012.04.037
- Humbird, D., Davis, R., Tao, L., Kinchin, C., Hsu, D., Aden, A., 2011. Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol: Dilute-Acid Pretreatment and Enzymatic Hydrolysis of Corn Stover, National Renewable Energy Laboratory.
- Jin, E., Mendis, G.P., Sutherland, J.W., 2019. Integrated sustainability assessment for a bioenergy system: A system dynamics model of switchgrass for cellulosic ethanol production in the U. S. midwest. J. Clean. Prod. 234, 503–520. https://doi.org/10.1016/j.jclepro.2019.06.205
- Kapanji, K.K., Haigh, K.F., Görgens, J.F., 2019. Techno-economic analysis of chemically catalysed lignocellulose biorefineries at a typical sugar mill : Sorbitol or glucaric acid

and electricity. Bioresour. Technol. 289, 121635.

https://doi.org/10.1016/j.biortech.2019.121635

- Mandegari, M.A., Farzad, S., Görgens, J.F., 2017a. Economic and environmental assessment of cellulosic ethanol production scenarios annexed to a typical sugar mill. Bioresour. Technol. 224, 314–326. https://doi.org/10.1016/j.biortech.2016.10.074
- Mandegari, M.A., Farzad, S., van Rensburg, E., Görgens, J.F., 2017b. Multi-criteria analysis of a biorefi nery for co-production of lactic acid and ethanol from sugarcane lignocellulose. Biofuels, Bioprod. Biorefining 11, 971–990. https://doi.org/10.1002/bbb
- Mokomele, T., Sousa, C., Balan, V., Rensburg, E. Van, Dale, B.E., Görgens, J.F., 2018. Ethanol production potential from AFEX <sup>™</sup> and steam - exploded sugarcane residues for sugarcane biorefineries. Biotechnol. Biofuels 11, 1–21. https://doi.org/10.1186/s13068-018-1130-z
- Moncada, J., Cardona, C.A., Higuita, J.C., Vélez, J.J., López-Suarez, F.E., 2016. Wood residue (Pinus patula bark) as an alternative feedstock for producing ethanol and furfural in Colombia: Experimental, techno-economic and environmental assessments. Chem. Eng. Sci. 140, 309–318. https://doi.org/10.1016/j.ces.2015.10.027
- Nhien, L.C., Long, N.V.D., Kim, S., Lee, M., 2016. Design and optimization of intensified
   biorefinery process for furfural production through a systematic procedure. Biochem.
   Eng. J. 116, 166–175. https://doi.org/10.1016/j.bej.2016.04.002
- Ntimbani, R.N., Farzad, S., Görgens, J.F., 2021. Furfural production from sugarcane bagasse along with co-production of ethanol from furfural residues. Biomass Convers. Biorefinery. https://doi.org/https://doi.org/10.1007/s13399-021-01313-3

- Özüdoğru, H.M.R., Haigh, K.F., Görgens, J.F., 2019. Techno-economic analysis of product biorefineries utilizing sugarcane lignocelluloses : Xylitol , citric acid and glutamic acid scenarios annexed to sugar mills with electricity co-production. Ind. Crop. Prod. 133, 259–268. https://doi.org/10.1016/j.indcrop.2019.03.015
- Petersen, A.M., Haigh, K., Görgens, J.F., 2014. Techno-economics of integrating bioethanol production from spent sulfite liquor for reduction of greenhouse gas emissions from sulfite pulping mills. Biotechnol. Biofuels 7, 1–14. https://doi.org/10.1186/s13068-014-0169-8
- Rosales-Calderon, O., Arantes, V., 2019. A review on commercial- scale high-value products that can be produced alongside cellulosic ethanol. Biotechnol. Biofuels 12, 1–58. https://doi.org/10.1186/s13068-019-1529-1
- Silva, J.F.L., Selicani, M.A., Junqueira, T.L., Klein, B.C., Vaz, S., Bonomi, A., 2017. Integrated furfural and first generation bioethanol production: Process simulation and technoeconomic analysis. Brazilian J. Chem. Eng. 34, 623–634. https://doi.org/10.1590/0104-6632.20170343s20150643
- Smithers, J., 2014. Review of sugarcane trash recovery systems for energy cogeneration in South Africa. Renew. Sustain. Energy Rev. 32, 915–925. https://doi.org/10.1016/j.rser.2014.01.042
- Yan, K., Wu, G., Lafleur, T., Jarvis, C., 2014. Production, properties and catalytic
   hydrogenation of furfural to fuel additives and value-added chemicals. Renew. Sustain.
   Energy Rev. 38, 663–676. https://doi.org/10.1016/j.rser.2014.07.003

Zeitsch, K.J.J., 2000. The chemistry and technology of furfural and its many by-products,

Sugar Series Vol. 13, Elsevier, The Netherlands. https://doi.org/10.1016/S1385-

8947(00)00182-0

Zhao, X., Liu, D., 2019. Multi-products co-production improves the economic feasibility of cellulosic ethanol : A case of Formiline pretreatment-based biore fi ning. Appl. Energy 250, 229–244.

## Chapter 6: Techno-economics of one-stage and two-stage furfural production from sugarcane lignocelluloses, with ethanol co-production

**Chapter to be submitted in:** Biofuels, Bioproducts & Biorefining (Biofpr), Impact Factor: 4.528

**Title:** Techno-economics of one-stage and two-stage furfural production from sugarcane lignocelluloses, with ethanol co-production

Authors: Rhulani N. Ntimbani, Somayeh Farzad, Johann F. Görgens

Declaration: This chapter will be submitted as a manuscript for publication in Biofuels,

Bioproducts & Biorefining (Biofpr) Journal

#### Objectives of this chapter in dissertation and findings

The study was focused on evaluating the technical and economic aspects of an integrated two-stage furfural and ethanol co-production employing steam explosion for biomass pretreatment, and to produce the hemicellulose hydrolysate used as furfural feed. Comparison of techno-economic aspects of the two-stage furfural integrated with ethanol co-production and the most promising one-stage furfural integrated with ethanol co-production biorefinery (Chapter 5) was also conducted.

The two-stage furfural production method is more suitable for ethanol co-production as it was able to achieve the lowest minimum ethanol selling price (0.73 US\$/L) compared to the most promising one-stage furfural and ethanol co-production biorefinery (1.14 US\$/L). The two-stage furfural and ethanol integrated biorefinery is well configured to benefit ethanol economics from an increase in production scale. The energy self-sufficient biorefinery reduces amount of feedstock available to the biorefinery, thereby, preventing the biorefinery from realising its full economic potential.

### **Declaration by the candidate:**

With regards to Chapter 6, page numbers 144-178 of this dissertation, the nature and scope

of my contributions were as follows:

Nature of contribution	Extent of contribution (%)
Simulation work planning	95
Executing simulations and techno-economics	100
Interpretation of results	90
Writing the chapter	100

The following co-authors have contributed to Chapter 6 pages 144-178 in the dissertation in the following manner:

Name	E-mail address	Nature of contribution	Extent of contribution (%)
		<ul> <li>Simulation work planning</li> </ul>	5
Somayeh Farzad	<u>sfarzad@sun.ac.za</u>	Interpretation of results	5
		<ul> <li>Reviewing chapter</li> </ul>	50
Johann Fordinand		• Interpretation of	5
Görgons	jgorgens@sun.ac.za	results	
Gugens		<ul> <li>Reviewing chapter</li> </ul>	50

Candidate signature:....

Date:....

Declaration with signature in possession of candidate and supervisor.

#### **Declaration by co-authors**

All authors read and approved this manuscript and hereby confirm that:

I. The declaration above accurately reflects the nature and extent of the contributions of the candidates and co-authors to Chapter 6, page numbers 144-178 in the dissertation,

II. No other authors contributed to Chapter 6, page numbers 144-178 in the dissertation beside those specified above, and

III. Potential conflicts of interest have been revealed to all interested parties and that are necessary arrangements have been made to use the material in Chapter 6 of the dissertation.

# Techno-economics of one-stage and two-stage methods for furfural production from sugarcane lignocelluloses, with ethanol co-production

Rhulani N. Ntimbani, Somayeh Farzad\*, Johann F. Görgens

Department of Process Engineering, Stellenbosch University, Private Bag X1, Stellenbosch 7602, South Africa

#### Abstract

Biorefinery scenarios c the two-stage and one-stage methods for furfural production, integrated with ethanol co-production, from sugarcane bagasse and harvest residue, to determine effect of process conditions on profitability, as reflected by the minimum ethanol selling price (MESP) at a fixed furfural selling price. Biorefineries with two-stage furfural production using low (Scenario 1), medium (Scenario 2) and high (Scenario 3) severity steam explosion pretreatment, and a preferred biorefinery with one-stage furfural production, were simulated in Aspen Plus® V8.8. The ethanol yield improvements from two-stage furfural production with ethanol co-production were outweighed by capital requirements that were 7-17% higher than the one-stage furfural production with ethanol co-production. Conversely, biorefineries with one-stage furfural production had increased heating demands (2034 vs. 741-1124 kW/tonne feed) and reduced ethanol yields (9 vs 15-21 kg/100 kg of feed) compared to two-stage. The required MESPs in the two-stage Scenario 2 (0.73 US\$/L) were decreased by 36% compared to the one-stage furfural-ethanol biorefinery (1.14 US\$/L). Scenario 1 and 3 were disadvantaged by lower ethanol yields (15 vs 21 kg/100 kg of feed) and higher capital investments (322-340 vs 310 million US\$) compared to Scenario 2. Optimization of process conditions, improving energy efficiency and maximising productivity within these energy self-sufficient facilities were critical to minimising the MESPs, regardless of associated increases in capital and operational costs.

Keywords: furfural, ethanol, lignocellulose, sugarcane bagasse, techno-economics

\*Corresponding author. Tel.: +27 21 808 9485; fax: +27 21 808 2059. E-mail address: sfarzad@sun.ac.za

#### 1 Introduction

The success of sustainable development involves reducing dependency on nonrenewable resources such as coal and oil (Cai et al., 2014; Prajapati et al., 2020). Lignocellulosic materials such as sugarcane bagasse and harvest residues are among the most abundantly available renewable resources (Smithers, 2014), and these biomass feedstocks offer the opportunities to reduce dependency on fossil-based feedstock (Jin et al., 2019; Prajapati et al., 2020). Specifically, lignocellulosic ethanol can act as a platform chemical used to derive a range of chemical/polymer products and can replace gasoline as fuel through blending or when used as is in ethanol compatible engines (Himmel et al., 1999; Jin et al., 2019). Similar to ethanol, the furan derivative, 2-methylfuran, can potentially replace gasoline and is derived from furfural, which is only produced from pentosans found in lignocelluosic biomass (Bohre et al., 2015). In addition to 2-methylfuran, furfural also presents opportunities as a platform chemical for derivation of a range of biochemicals and fuel additives (Bohre et al., 2015; Yan et al., 2014). Therefore, furfural and ethanol are some of the promising bioproducts that offer alternatives to fossil-based products.

Furfural and ethanol co-production provides an opportunity for efficient utilization of biomass as both the cellulosic and hemicellulosic components of lignocellulose are converted to bioproducts, with lignin serving as a supplement fuel for the boiler (Cai et al., 2014; Farzad

et al., 2017; Moncada et al., 2016). The one-stage (direct) method of furfural production from lignocelluloses is industrially well-established, and may be suitable for ethanol co-production from the cellulose-rich residues (solids) that remain after hemicelluloses conversion (Cai et al., 2014; Silva et al., 2017). The one-stage furfural process may therefore serve a dual purpose of both furfural production and lignocellulose pretreatment for subsequent ethanol production (Avci et al., 2013; Mesa et al., 2014; Ntimbani et al., 2021a).

Nevertheless, the one-stage furfural process is associated with high-energy demands and promotes cellulose degradation due to severe process conditions (Cai et al., 2014; Xing et al., 2011; Ntimbani et al, 2021a). The one-stage furfural process also tends to produce yeast inhibitors and favour formation of pseudo-lignin, which negatively affect subsequent enzymatic hydrolysis and fermentation processes (Hu et al., 2012).

Alternatively, in the two-stage furfural production, where the lignocelluloses are firstly fractionated into a hemicellulosic sugar hydrolysate and cellu-lignin solids, prior to conversion of hemicelluloses into furfural, offers an opportunity for higher furfural and ethanol yields (Cai et al., 2014; Dashtban et al., 2012). For instance, steam explosion processing (205°C, 13.5 min) of sugarcane bagasse permits production of xylose rich hydrolysates and enzymatically digestible solids, suitable for furfural and ethanol production, respectively, with minimal cellulose degradation and formation of yeast inhibitors (Mokomele et al., 2018). The two-stage method allows separate optimisation of hemicellulose hydrolysate production, as feedstock for furfural production, together with maximising the preservation, digestibility and suitability of the cellulose-rich solids as ethanol feedstock. While the two-stage furfural methods provides an opportunity to obtain higher yields of furfural and ethanol, pretreatment of the lignocellulose in a dedicated process step remains capital and energy

intensive, which is avoided in the one-stage furfural production. Hence, techno-economic studies are required to determine whether the two-stage furfural process with ethanol co-production is economically more attractive than the one-stage furfural process.

Previous techno-economic studies considering the two-stage furfural and ethanol coproduction from lignocelluloses have employed organic solvents (i.e., chloroform, toluene, tetrahydrofuran) for furfural separation from the hydrolysate reaction mixture, which makes the overall process less attractive from an environmental perspective (Farzad et al., 2017; Xing et al., 2011; Zang et al., 2020; Zhao and Liu, 2019). Moreover, the need to recover the organic solvents require capital investment and energy inputs to avoid costs of purchasing fresh organic solvents (Zhao and Liu, 2019). Inclusion of a water-washing stage to remove yeast inhibitors from solid residues after pretreatment, is a common feature in integrated two-stage furfural and ethanol process flowsheets (Hernández et al., 2014; Moncada et al., 2016; Zhao and Liu, 2019). Employing washing for solids detoxification requires large amounts of water that require substantial amounts of process energy for downstream removal and treatment, to meet environmental regulation requirements (Mokomele et al., 2018; Shi et al., 2019).

The need for removal of yeast inhibitors can be avoided by using inhibitor resistant yeast (Mokomele et al., 2018; Watanabe et al., 2019), while the use of organic solvents for furfural separation can be replaced by using a vapour releasing reactor, followed by conventional furfural azeotropic steam distillation (Liu et al., 2018; Silva et al., 2017; Zeitsch, 2000). In view of this, the present study aims to conduct techno-economic assessment of two-stage furfural production using vapour releasing reactor and ethanol co-production employing industrially available yeast without the need for washing the pretreated solids prior to fermentation. The

study also provides a comparison of the two-stage and one-stage furfural process integrated with ethanol co-production to determine the most economically worthwhile biorefinery configuration for furfural and ethanol co-production. Biorefineries for alternative process configurations were designed to be energy self-sufficient, to avoid the use of external energy sources that are frequently provided by fossil fuels, which will not achieve the environmental objectives of these products.

#### 2 Process simulation and economic evaluation methodology

Aspen Plus<sup>®</sup> V8.8 (Aspen Technology Inc., USA) was used to simulate the two-stage furfural and ethanol co-production biorefineries, whereby steam explosion was employed to produce digestible solids for ethanol production and xylose rich hydrolysate utilised as furfural feedstock. A total of three biorefinery scenarios were developed based on data from previous works (Mokomele et al., 2018; Neves et al., 2016), own furfural experimental data presented in supplementary data Table S.1-2 and other research work (Hamman et al., 2020; Mokomele et al., 2019), where similar feedstock have been investigated. A fourth simulation considered the preferred biorefinery that combined one-stage furfural production with ethanol co-production, as identified previously (Ntimbani et al., 2021b). The profitability of each biorefinery was indicated by internal rate of return (IRR), as well as the minimum ethanol selling prices (MESP) at various discount rates or IRRs (10, 15, 20%), with the selling price of furfural fixed at market prices (Petersen et al., 2014).

Dry biomass availability of 65 tonne/hr comprised of sugarcane bagasse (70 wt.%) and harvest residues (30 wt.%) with final feedstock mass composition of 40.7% cellulose, 27.1% hemicellulose, 21.9 % lignin, 6.75% extractives and 3.5% ash was used as feedstock for the

sugarcane biorefinery annexed to an existing sugar mill, as in previous studies (Farzad et al., 2017; Kapanji et al., 2019; Özüdoğru et al., 2019). This feedstock was based on data from a typical South African sugar mill (Farzad et al., 2017; Mandegari et al., 2017). The adapted composition was assumed to be applicable to the feedstock mixture comprised of sugarcane bagasse and harvest residues (Mandegari et al., 2017).

Considering the nature of the biomass feedstock, the Electrolyte non-random twoliquid thermodynamic model was selected for Aspen simulation because it is appropriate for partially immiscible systems and non-ideal mixtures (Gebreyohannes et al., 2014; Mandegari et al., 2017). The properties of biorefinery compounds not available in Aspen Plus<sup>®</sup> databases were either calculated or estimated and the known properties were exported into properties module (Mandegari et al., 2017; Moncada et al., 2016).

#### 2.1 Scenario Description and Process flowsheet development

The two-stage furfural and ethanol co-production was investigated by considering three biorefinery scenarios with similar process flowsheets, as provided in Figure 6.1, only differing in the lignocellulose pretreatment conditions, which subsequently affected both furfural and ethanol production (Mokomele et al., 2018; Neves et al., 2016; Hamman et al., 2020; Mokomele et al., 2019). As reported in previous studies (Mokomele et al., 2018; Neves et al., 2016), steam explosion of sugarcane lignocelluloses in the temperature range of 190-215°C and residence time of 5-13.5 minutes can simultaneously produce a hemicellulosehydrolysate for furfural production and cellulose-rich solids suitable for ethanol production by hydrolysis-fermentation. Furfural yields for the two-stage process was estimated from furfural experimental work presented in supplementary data Table S.1-2, using hydrolysates

produced from steam explosion pretreatment under these conditions (Hamman et al., 2020). The selected data for simulation is summarised in Table 6.1. Furfural produced during the steam explosion itself was also recovered into the furfural vapour product, which the furfural reactor was designed to release (Metkar et al., 2015; Silva et al., 2017).

The biorefinery scenarios were designed to be energy self-sufficient, where the energy demands (steam and electricity) of both the biorefinery itself and the sugar mill to which it is annexed, were supplied by a new boiler fed with lignin residues and a "bypass" portion of the available lignocellulosis; the required bypass was determined by trial and error in Aspen Plus<sup>®</sup> simulations (Farzad et al., 2017; Kapanji et al., 2019) (Figure 6.1). The existing sugar mill boiler was therefore scrapped and replaced with a new one capable of supplying both the sugar mill and the biorefinery (Kapanji et al., 2019). Xylan and xylose available in Aspen Plus<sup>®</sup> databanks were selected to represent pentosans and pentose sugars in simulation models, respectively (Hossain et al., 2019). Cellulose and glucose available in Aspen Plus<sup>®</sup> databanks were selected to simulate hexosans and hexose sugars (Hossain et al., 2019), respectively, with acid insoluble degradation products simulated as tar also available in Aspen Plus<sup>®</sup> databanks (Humbird et al., 2011).



## Figure 6.1: Two-stage furfural and ethanol co-production biorefinery process flow diagrams (PFD) including boiler, power and steam generation

Table 6.1: Steam pretreatment, furfural reactor and fermentation bioreactor operating conditions including glucan and xylan hydrolysis as well as furfural and ethanol yield

Scenario	1	2	3					
Steam explosion pretreatment								
Reference	(Neves et al., 2016)	(Mokomele et al., 2018)	(Hamman et al., 2020)					
Temperature (°C)	190	205	215					
glucan to glucose	5.23	6.63	25.40					
Xylan to xylose	76.07	64.00	46.32					
Furfural Production using	steam explosion hydrolys	ates (detailed results prese	nted in Table S.1-2 of					
	supplement	ary data)						
Scenario	1	2	3					
Temperature (°C)	180	180	160					
H2SO4 (wt.%)	2	2	2					
Furfural yield based on pentosans (% theoretical)	64.24	66.91	47.24					
	Simultaneous Saccharific	ation & Fermentation						
Scenario	1	2	3					
Reference	Neves et al., 2016	Mokomele et al., 2019)	(Hamman et al., 2020)					
Temperature (°C)	35	35	35					
Ethanol yield %	67	92	63					
Fermentation yeast	Thermosac Dry	CelluX™4	M2n					

#### 2.1.1 Steam explosion pretreatment

Steam explosion was selected for biomass fractionation for the two-stage furfural production process, at it has been previously shown to produce both a xylose rich hydrolysate for furfural production, and enzymatically digestible solids for ethanol production, without the addition of any reagents besides steam (Mokomele et al., 2018). The steam explosion unit is shown in Figure 6.2, which includes a representation of bioethanol production (hydrolysis & fermentation), furfural production, purification and recovery sections of Aspen Plus<sup>®</sup> flowsheet.



Figure 6.2: Aspen Plus<sup>®</sup> screenshot of the steam explosion and ethanol production as well as furfural production, purification and recovery

#### 2.1.2 Bioethanol production, purification and recovery

Steam exploded solids were separated from liquid hydrolysate using pneumatic press (Humbird et al., 2011) and used as for subsequent ethanol production using the simultaneous saccharification and fermentation (SSF) (Table 6.1). Based on previous experimental work, it was assumed that 26 mg protein/g dry solids (19 Cellic CTec2<sup>®</sup> and 7 mg Cellic HTec2<sup>®</sup>) would

be sufficient to yield fermentation sugars in all Scenarios considered (Mokomele et al., 2018). The produced ethanol was purified and recovered using distillation (beer and rectification) columns followed by molecular adsorption and sieving that yield  $\geq$ 99.50 wt.% ethanol product (Humbird et al., 2011; Mandegari et al., 2017). Ethanol rich vapour side stream was drawn from the beer column and fed into the rectification column, where the vapour top product containing  $\geq$ 92.5 wt.% ethanol is recovered and sent to the molecular adsorption and sieving section to recover the final ethanol product (Humbird et al., 2011; Mandegari et al., 2017).

#### 2.1.3 Furfural production, recovery and purification

Furfural production was carried out using hydrolysate from steam explosion in a furfural vapour releasing reactor (de Jong and Marcotullio, 2010; Silva et al., 2017), with the addition of 2 wt.% sulphuric acid at 180°C (Scenario 1 and 2) and 160°C (Scenario 3), according to furfural experimental work presented in Table S.1-2 of supplementary data. Furfural was recovered in the vapour product released by the furfural reactor (furfural vapour stream from pretreatment was also included), which was sent for purification and recovery by distillation train comprised of three columns as shown in Figure 6.2 (Nhien et al., 2016; Silva et al., 2017; Zeitsch, 2000). The first azeotropic column serves the purposes of removing water from the furfural product and has a vapour side product rich in furfural with volatile components such as formic acid removed through the top product stream (Nhien et al., 2016; Silva et al., 2017; Zeitsch, 2000). The second column is used to recover furfural that escapes through the top product stream of the first column, while its bottoms product (containing mostly furfural) is sent to a decanter, together with the side vapour product from the first column (Nhien et al., 2016; Silva et al., 2017; Silva et al., 2017; Zeitsch, 2000). Furfural rich phase from the decanter is sent to the

third and final distillation column, which yields  $\geq$ 99.50wt% furfural recovered from the bottoms products, while the top product is recycled back to the decanter to avoid furfural loss to waste streams (Nhien et al., 2016; Silva et al., 2017; Zeitsch, 2000). The water rich phase from the decanter is recycled back into the first distillation as a way of minimising furfural losses to waste streams (Nhien et al., 2016; Silva et al., 2017; Zeitsch, 2000).

#### 2.1.4 Evaporation unit

Residual solids from the ethanol production section were dewatered in the evaporation section prior to being sent to the boiler to serve as supplement fuel (Farzad et al., 2017; Mandegari et al., 2017). A multiple effect evaporator comprised of a flash drum and a pneumatic pressure filter were used to separate the wet solids and the liquid was concentrated to produce a syrup also used as supplement boiler fuel with the remaining liquid treated and utilised as process water (Farzad et al., 2017; Mandegari et al., 2017).

#### 2.1.5 Wastewater treatment (WWT) unit

All wastewater streams were treated in the wastewater treatment unit (WWT) prior to being released to prevent environmental pollution (Farzad et al., 2017; Mandegari et al., 2017). The treated water from the WWT unit was assumed to be reusable by the biorefinery and sugar mill, as a way of minimising required amount of fresh make-up water (Mandegari et al., 2017). The flowsheet of the WWT unit that was adapted for this work is documented in previous research work (Mandegari et al., 2017).

#### 2.1.6 Combined heat and power (CHP) unit

The new combined heat and power plant consist of a combustor, boiler and condensing-extraction steam turbines (CEST) (Farzad et al., 2017; Mandegari et al., 2017).

Boiler fuel consisted of biomass residues and waste organic compounds recovered from the biorefinery and a fraction of the available lignocelluloses, i.e. the "bypass," determined through trial and error in Aspen Plus<sup>®</sup>. The CEST provided means to extract steam at different conditions (temperature and pressure) as required by the sugar mill and biorefinery, and also produced minimal electricity as a by-product of which the surplus was assumed to be sold to the grid as a by-product (Farzad et al., 2017; Kapanji et al., 2019; Mandegari et al., 2017).

#### 2.2 Economic evaluation

Aspen Plus<sup>®</sup> Economic Evaluator and literature data were used to estimate the purchased and installed cost of equipment, as well as total production costs (variable and fixed operating) from mass and energy balances generated in Aspen Plus<sup>®</sup> simulations of the biorefinery scenarios (Humbird et al., 2011; Moncada et al., 2016). Equipment costs for boilers, turbo-expanders, generators, reactors, waste water treatment basins were estimated using technical data contained in the National Renewable Energy Laboratory report (Humbird et al., 2011) and other research work (Mandegari et al., 2017), since Aspen Economic Analyser cost estimation for these process units is not precise (Mandegari et al., 2017; Moncada et al., 2016).

Total production cost (TCOP) included feedstock cost, process reagents waste disposal as part of variable cost and fixed costs that included labour, plant maintenance and property insurance. South African tax rate (28%) was accounted for as an additional economic parameter since the biorefinery was based on typical South African sugar mill and biomass availability (Farzad et al., 2017; Kapanji et al., 2019). Cost estimation formulas together with respective installation factors and scaling exponents were used to estimate purchased and

installed cost of the equipment from published data (Humbird et al., 2011). Straight line depreciation method was assumed to account for property, plant and equipment depreciation over five years at 20% per annum (Kapanji et al., 2019; Nieder-Heitmann et al., 2018).

Economic viability of the investigated biorefinery Scenarios were indicated by the internal rate of return (IRR) computed using market prices of ethanol and furfural given in Table 6.2 (Farzad et al., 2017; Mandegari et al., 2017). Minimum ethanol selling prices (MESP) of each scenario at 10, 15, and 20% discount rates or IRRs were computed to evaluate the extent of furfural co-production benefit on ethanol economics (Petersen et al., 2014). The robustness of the biorefineries was evaluated through sensitivity analysis considering effects of total capital investment costs (TCI), total production costs (TCOP), furfural and ethanol selling price, electricity price, maintenance costs, working capital and income tax on IRR (Farzad et al., 2017). A summary of economic parameters and methods applied for economic evaluation is provided in Table 6.2.

Parameters	Value
Annual operating hours	6480 h
Project life	25 years
Finance	100% equity
Income tax rate	28%
Depreciation	Straight line over 5 years (20% per year)
Salvage value	0
Construction period	2 years
% Spent in year -2	10%
% Spent in year -1	60%
% Spent in year 0	30%
Working capital	5% of fixed capital investment
Start-up time	2 years
First year production capacity	50%
Second year production capacity	75%
Electricity selling price	0.08 US\$/kWh
Furfural price <sup>1</sup>	2200 US\$/tonne
Ethanol price <sup>2</sup>	0.596 US\$/L
Enzymes cost <sup>3</sup>	1000 US\$/tonne
Cost year for analysis	2018

Table 6.2: Economic analysis parameters (Mandegari et al., 2017; Nieder-Heitmann et al., 2018).

<sup>1</sup>(Rosales-Calderon and Arantes, 2019; Yan et al., 2014) <sup>2</sup>(Farzad et al., 2017; Mandegari et al., 2017) <sup>3</sup>(Gubicza et al., 2016)

#### 3 Results and discussion

#### 3.1 Mass and energy balance

The overall mass and energy balances demonstrated that operating conditions significantly influenced the energy demands of the different biorefinery scenarios, as reflected in the required bypass of the lignocellulose feedstocks to boilers (Table 6.3). Detailed mass and energy balance results from Aspen Plus® simulations are provided in Tables S.3-S.26 of supplementary data together with screenshots of Aspen Plus® flowsheet diagrams of the simulated biorefinery sections provided in Figure S.1-S.8. Among the biorefineries with two-stage furfural production, Scenario 2 had the highest heating energy demand per tonne of feedstock (1124 kW/tonne feedstock) compared to Scenario 1 (876 kW/tonne feedstock) and Scenario 3 (741 kW/tonne feedstock) as reported in Figure 6.3. This can be attributed to

the larger mass flows of both ethanol and furfural per tonne of feedstock because of higher of furfural and ethanol yields of 67% and 92%, respectively, when compared to furfural yields of 64% and 47% in Scenario 1 and 3 with corresponding ethanol yields of 67% and 63%, respectively. Larger mass flows of furfural or ethanol results in higher heating and cooling demand due to energy intensive process of furfural and ethanol separation via distillation (Cardona et al., 2010; Nhien et al., 2016). Cooling duties were mainly carried out in the furfural and ethanol distillation processes by condensers, therefore, Scenario 2 was associated with higher cooling duties (1960 kW/kg of feedstock) due to the larger mass flows of both ethanol and furfural compared to Scenario 1 and 3. Power duties followed a similar trend as cooling and heating duties, but were smaller (21-30 kW/tonne of feedstock) compared to heating demands in all the two-stage biorefinery scenarios as the majority of heating and cooling is provided using steam and cooling water.



Figure 6.3: Heating, cooling and power duties for integrated furfural and ethanol coproduction biorefineries.

The two-stage furfural process integrated with ethanol co-production scenarios have better energy efficiency than the one-stage furfural process integrated with ethanol coproduction. The two-stage furfural and ethanol integrated biorefineries required heating duty of 741-1124 kW/tonne of feed, while the one-stage furfural and ethanol integrated biorefinery required 2034 kW/tonne of feed (Figure 6.3). This also supported by the fact that the one-stage furfural and ethanol integrated biorefinery required a higher feed bypass (58%) to boiler compared to the two-stage furfural and ethanol integrated biorefineries (30-50%). The need for continuous vapour-phase stripping of furfural in the one-stage process to avoid furfural degradation was mainly responsible for the higher energy demands (Cai et al., 2014; Dashtban et al., 2012; Zeitsch, 2000). The two-stage process avoids the need for continuous steam stripping, but still avoids furfural degradation by first separating the hemicellulose sugars from cellu-lignin followed by conversion to furfural in a separate processing unit containing less amounts of degradation products (Cai et al., 2014; Yoo et al., 2012).

In an energy self-sufficient system, the production rate of ethanol is not only determined by the rate of feedstock supply, and yield of ethanol on feedstock, but also by the energy demands of the chosen conversion process, as this determines what portion of total lignocellulose feed is available for ethanol production, with the rest going to the boiler. The high heating and power duty requirements in Scenario 2 negatively affected the overall ethanol (6948 kg/hr) and furfural (2945 kg/hr) production rates, since they resulted in highest bypass (50%) of the two-stage scenarios (Table 6.3). The high bypass in Scenario 2 restricted ethanol production (6948 kg/hr) between production rates achieved in Scenario 1 (6248 kg/hr) and Scenario 3 (7112 kg/hr), regardless of higher ethanol yields (21.4 kg/tonne of dry

feed). The highest overall mass flow rates of ethanol (7112 kg/hr) was achieved in Scenario 3 as it had larger amount of feedstock available to the biorefinery (30 % bypass), although ethanol yield was only 15.6 kg/tonne of dry feed. The low ethanol yields (15.0 kg/ton of dry feed) and feed bypass of 36% in Scenario 1 resulted in the lowest ethanol production rate 6248 kg/hr. Bypass of 36% furfural yield of 9.1 kg/tonne of dry feed resulted in the overall furfural production rate (3248 kg/hr) of Scenario 1 being the highest. Low bypass of 30% in Scenario 3 could not compensate for low furfural yield of 4.7 kg/tonne of dry feed, as such, the lowest furfural production rate (2122 kg/hr) occurred in Scenario 3.

	Unit	Scenario 1	Scenario 2	Scenario 3	(Ntimbani et al., 2021) (One-stage FF & EtOH)
Feedstock (50% moisture)	tonne/hr	113.53	113.53	113.53	113.53
Bypass to boiler	tonne/hr	40.87	56.76	34.06	65.85
Feed bypass % to boiler	%	36.00	50.00	30.00	58.00
To biorefinery	tonne/hr	72.66	56.76	79.47	47.68
Products					
Ethanol	kg/hr	6247.96	6948.05	7111.76	2452.00
Furfural	kg/hr	3248.34	2944.79	2121.54	3754.00
Ethanol/Dry Feedstock	kg/tonne	15.02	21.38	15.63	8.98
Furfural/Dry Feedstock	kg/tonne	7.81	9.06	4.66	13.75
Surplus electricity	MW	16.73	17.69	16.45	21.63
Steam used by StEX or FF reactor/feedstock	kg/tonne	160	220	261	493
Total HPS demand	kg/hr	14798	15336	20774	29415
Total LPS demand	kg/hr	99207	99599	92315	128192

Table 6.3: Overall mass and energy balance of the studied biorefinery Scenarios

FF-furfural; StEX-steam explosion pretreatment; EtOH-ethanol; LPS-low pressure steam (230°C & 9.5 atm); HPS-High pressure steam (266°C & 13 atm); One-stage FF (170°C & 0.5wt.% H<sub>2</sub>SO<sub>4</sub>) & Ethanol (Ntimbani et al., 2021).

#### 3.2 Economic analysis

Low severity steam explosion pretreatment conditions (Scenario 1) resulted in a biorefinery that had higher furfural revenue (46.3 million US\$/yr) compared to 41.9 (Scenario 2) and 30.2 million US\$/yr (Scenario 3) as shown in Figure 6.4. The lower bypass requirements in Scenario 1 (36%) compared to Scenario 2 (50%) resulted in higher furfural revenue although the highest furfural yield was achieved in Scenario 2. Furfural revenues generated in Scenario 3 were negatively affected by low furfural yield (4.7 kg/tonne feed) and was not boosted by low bypass (30%). While there were clear differences in furfural revenue, ethanol revenues were similar in medium severity conditions (Scenario 2; 34.3 million US\$/yr) and high severity conditions (Scenario 3; 35.2 million US\$/yr). The medium severity conditions (Scenario 2) resulted in the highest ethanol yield (21.4 kg/tonne of dry feed), but the required 50% bypass resulted in ethanol production rate of 6948 kg/hr that was similar to Scenario 3 (7112 kg/hr).



Figure 6.4: Annual ethanol and furfural revenues for investigated biorefinery scenarios.

The improved ethanol yields from steam explosion pretreated biomass in the two-stage furfural and ethanol biorefineries increased the total capital investment (TCI) requirements to 310-340 million US\$, compared to the most promising one-stage furfural and ethanol biorefinery (291 million US\$), as reported in Table 6.4. The profitability of the one-stage furfural and ethanol biorefinery was mainly affected by energy requirements that required high feed bypass of 58% (Ntimbani et al., 2021b) compared to 30-50% feed bypass required in the two-stage furfural and ethanol integrated biorefineries. Due to the negative effects of capital and energy requirements on profitability, the IRR (13.59%) of the most promising twostage furfural and ethanol biorefinery (Scenario 2) was comparable to the IRR (12.78%) of the promising one-stage furfural and ethanol biorefinery (Ntimbani et al., 2021b).

Since production costs (TCOP) and capital investment (TCI) negatively affect IRR, both the low TCOP (19.85 million US\$/yr) and TCI (310.23 million US\$) benefitted the process economics in Scenario 2. The benefits of higher production rates in Scenario 1 and 3 were also outweighed by the higher TCOP (20.20-20.74 million US\$/yr) and TCI (322.58 -340.46 million US\$) as reported in Table 6.4. The IRR (13.59%) value for Scenario 2 was comparable to the IRR (13.11%) of Scenario 1 and higher than the IRR (10.07%) of Scenario 3. Therefore, the low TCI (310.23 million US\$) and TCOP (19.85 million US\$/yr) in Scenario 2 together with higher yields of ethanol (21.38 kg/tonne of feed) and furfural (9.06 kg/tonne of feed) allowed the cash flows to generate a slightly higher IRR (13.59%) than Scenario 1 (IRR=13.11%). A higher overall furfural production rate was attained in Scenario 1 (3248 kg/hr) compared to Scenario 2 (2944 kg/hr), although the lower yields of ethanol (15.03 kg/tonne of feed) and furfural (7.81 kg/tonne of feed), coupled with high TCI (322.58 million US\$) and TCOP (20.20 US\$/yr), resulted in a weaker financial performance for Scenario 1, compared to Scenario 2. The profitability of Scenario 3 was mainly affected by low furfural yield (4.66 kg/tonne of feed)

and high TCI (340.46 million US\$).

Scenarios	Process description	TCI (US\$)	TCOP (million US\$/year)	Ethanol/Dry Feedstock (kg/tonne)	Furfural/Dry Feedstock (kg/tonne)	IRR (%)	IRR (%), no electricity sales
Scenario 1	StEx at 190°C, FF reactor 180°C & 2.0wt.% H <sub>2</sub> SO <sub>4</sub>	322.58	20.20	15.02	7.81	13.11	11.43
Scenario 2	StEx at 205°C, FF reactor 180°C & 2.0wt.% $H_2SO_4$	310.23	19.85	21.38	9.06	13.59	11.78
Scenario 3	StEx at 215°C, FF reactor 160°C & 2.0wt.% H <sub>2</sub> SO <sub>4</sub>	340.46	20.74	15.63	4.66	10.07	8.29
(Ntimbani et al., 2021)	One-stage FF (170°C & 0.5wt.% H₂SO₄) & Ethanol	290.79	19.36	8.98	13.75	12.78	10.30

### Table 6.4: Key economic results for investigated furfural and ethanol biorefineries from lignocellulose at 2018 cost year of analysis

StEx - steam explosion pretreatment; FF - furfural; TCI - total capital investment; TCOP - total cost of production

Biorefineries with lower yields of ethanol invariably have a greater reliance on furfural for profitability, which is then also reflected in higher MESPs for these scenarios. The net revenue of the previously investigated one-stage furfural and ethanol co-production biorefinery (Ntimbani et al., 2021b) were predominantly from furfural sales due to high furfural yield (13.75 kg/tonne feed) and low ethanol yield (8.98 kg/tonne feed) (Table 6.5). Thus, the low ethanol yield needed to correspond to higher ethanol selling prices (1.14 and 2.54 US\$/L) in order to reach 15 and 20% IRR values. The high bypass (58%) in the one-stage also disadvantaged the one-stage furfural-ethanol biorefinery as it negatively affected biorefinery feed, production volumes and consequently net revenues. In contrast, the high ethanol yields (15-21 kg/tonne feed) and lower bypass (30-50%) rendered the two-stage furfural-ethanol co-production biorefineries well configured to improve ethanol economics, as indicated by lower MESPs in Scenario 1 (0.80 and 1.41 US\$/L), Scenario 2 (0.73 and 1.25 US\$/L) and Scenario 3 (1.05 and 1.62 US\$/L) at 15 and 20% IRR values. Improvement of MESPs in Scenario 2 was 36-51% compared to MESPs attained in the previously investigated (Ntimbani et al., 2021b) one-stage furfural co-production biorefinery Table 6.5. The IRR values for two-stage furfural and ethanol integrated biorefineries reported in Table 6.4 have a similar trend to MESPs values reported in Table 6.5 as expected.

Table 6.5: Minimum ethanol selling price (MESP) at various discount rates (IRR) for all the ethanol producing biorefinery Scenarios with and without electricity credit

discount rate % (IRR)	10.00	15.00	20.00	10.00	15.00	20.00
	MESP (US	\$/L) with electri	city credit	MESP (US\$/	L) without elec	tricity credit
Scenario 1	0.29	0.80	1.41	0.46	0.96	1.57
Scenario 2	0.29	0.73	1.25	0.45	0.88	1.41
Scenario 3	0.59	1.05	1.62	0.73	1.20	1.77
(Ntimbani et al. <i>,</i> 2021b) <sup>1</sup>	0.59	0.83	1.13	0.67	0.91	1.21
(Ntimbani et al., 2021b)²	-0.02	1.14	2.54	0.53	1.69	3.09

<sup>1</sup>Steam explosion at 205°C followed by whole slurry fermentation to produce ethanol;

<sup>2</sup>One-stage furfural (170°C & 0.5 wt.%  $H_2SO_4$ ) and ethanol co-production, negative MESP value meant that IRR could be achieved without ethanol sales.

#### 3.3 Economic sensitivity analysis

A sensitivity analysis was conducted to consider the economies of scale benefits associated with increasing the production scale of the two-stage and one-stage furfural production biorefineries. An increase in the production scale of 25% in the sugarcane mill and integrated furfural biorefinery provided the greatest economic benefit to Scenario 1, compared to the other two-stage biorefineries, reflected by a 24% reduction in MESPs (1.41 to 1.07 US\$/L), compared to 21% in Scenario 2 (1.25 to 0.99 US\$/L) and 16% in Scenario 3 (1.62 to 1.37 US\$/L) at 20% IRR (Table 6.6). The overall furfural production rate in Scenario 1

(3248 kg/hr) was 8.5% higher than furfural in Scenario 2 (2944 kg/hr) due to differences in yield and required bypass to boiler. Therefore, considering similarities in TCOPs (19.85-20.20 million US\$/yr), increasing production scale increased the net revenue of Scenario 1 more than Scenario 2. Although increased production scale improved MESPs (0.54 and 1.07 US\$/L) of Scenario 1 more, the lowest MESPs (0.51 and 0.99 US\$/L) corresponding to 15 and 20% IRR values were achieved in Scenario 2 (Table 6.6), which was the most profitable biorefinery scenario. Scenario 3 had the least improvement in MESPs because of low furfural yield (4.66 kg/tonne of feed), which could not be compensated by lower feed bypass (30%) to the boiler to generate higher overall furfural production rate (2121 kg/hr).

The high ethanol yield (92%) coupled with low TCOP (19.85 million US\$/yr) and TCI (310.23 million US\$) provided improved economic performances for Scenario 2 (two-stage furfural-ethanol biorefinery) compared to the one-stage furfural-ethanol co-production biorefinery (Ntimbani et al., in press) when production scale was increased by 25%. The required MESPs of Scenario 2 (0.51 and 0.99 US\$/L) were 27-48% lower than MESPs (0.70 and 1.91 US\$/L) required to attain 15 and 20% IRR in the one-stage furfural-ethanol biorefinery (Ntimbani et al., in press). The weaker economic performances of the one stage biorefinery was again attributed to lower product yields and higher energy demands, which could not be overcome by economies of scale benefits at larger scales.

discount rate % (IRR)	10.00	15.00	20.00	10.00	15.00	20.00
	MESP (US	\$/L) with electr	icity credit	MESP (US\$/	L) without elec	tricity credit
Scenario 1	0.10	0.54	1.07	0.29	0.72	1.25
Scenario 2	0.12	0.51	0.99	0.30	0.69	1.17
Scenario 3	0.42	0.85	1.37	0.59	1.02	1.54
Ntimbani et al., 2021b <sup>1</sup>	0.56	0.80	1.10	0.66	0.90	1.19
Ntimbani et al., 2021b <sup>2</sup>	-0.29	0.70	1.91	0.28	1.27	2.48

#### Table 6.6: Effect of scale on minimum ethanol selling price (MESP) at various discount rates (IRR).

<sup>1</sup>Steam explosion at 205°C followed by whole slurry fermentation to produce ethanol; <sup>2</sup>One-stage furfural (170°C & 0.5 wt.%  $H_2SO_4$ ) and ethanol co-production, negative MESP value meant that IRR could be achieved without ethanol sales.

Economic sensitivity analysis results in Figure 6.5 confirmed that the two-stage furfuralethanol biorefineries were more sensitive to the capital investment costs as indicated by the largest increases (3.32-3.87%) and decreases (2.26-2.64%) in IRR values as a result of 25% decrease and increase in capital investment costs, respectively. The economic sensitivity analysis results show that profitability of the furfural and ethanol integrated biorefinery biorefineries do not change linearly with an increase or decrease in capital costs as also demonstrated on tornado charts in previous studies (Farzad et al., 2017; Humbird et al., 2011; Nieder-Heitmann et al., 2018). The TCI of the two-stage furfural-ethanol co-production can be reduced through process intensification considering replacement of the furfural reactor and the first azeotropic furfural separation column with a reactive distillation column (Metkar et al., 2015), considering that the furfural feed is the liquid hydrolysate without solids.

In terms of product prices, the IRRs of the two-stage furfural-ethanol biorefineries were less sensitive to furfural price fluctuations than the most promising one-stage furfural-ethanol biorefinery. The IRR values of the two-stage furfural-ethanol biorefineries varied by 1.47-2.26% (Figure 6.5) compared to 2.68-2.98% in one-stage furfural-ethanol biorefinery
(Ntimbani et al., in press) when furfural price was increased or decreased by 25%. The profitability of the most promising one-stage furfural-ethanol biorefinery was more dependent on furfural sales due to higher ethanol yield (13.75 kg/tonne feed) achieved compared to the ethanol yields (4.66-9.06 kg/tonne feed) achieved in the two-stage furfural-ethanol biorefineries.

Ethanol price fluctuations have more potential to negatively affect the two-stage furfural-ethanol biorefineries than the most promising one-stage furfural-ethanol biorefinery. The profitability of the one-stage furfural-ethanol biorefinery was less dependent on ethanol sales due to lower ethanol yield (8.98 kg/tonne feed) achieved compared to the ethanol yields (15.02-21.38 kg/tonne feed) achieved in the two-stage furfural-ethanol biorefineries. The IRR values of the two-stage furfural-ethanol biorefineries varied by 1.41-1.84% (Figure 6.5) compared to 0.62-0.64% in one-stage furfural-ethanol biorefinery (Ntimbani et al., in press) when ethanol price was increased or decreased by 25%.

Overall, the biorefinery in Scenario 2 was more robust because the profitability indicated by IRR could not be surpassed by the IRRs of the other Scenarios investigated regardless of any changes imposed as shown in Figure 6.5. For instance, the lowest IRR in Scenario 2 is 10.95%, which could occur due to increase in TCI that have the largest influence in profitability, whereas the lowest IRRs for Scenario 1 and Scenario 2 were 10.52% and 7.81% ,respectively, when considering the effects posed by increase in TCI. The less excess biomass accommodated by process units due to high yields of both furfural (9.06 kg/tonne of feed) and ethanol (21.4 kg/tonne of feed) in Scenario 2 resulted in optimal equipment sizing and consequently lower TCI (310 million US\$), thereby making the two stage furfural-ethanol co-production biorefinery in Scenario 2 more superior in economic terms.

169



Figure 6.5: Economic sensitivity analysis of the studied furfural and ethanol co-production Scenarios.

#### 4 Conclusions

Energy demands have a larger effect on process economics than product yields as shown by lower MESPs for the two-stage furfural and ethanol co-production biorefineries which required less amount of energy compared to the one-stage furfural and ethanol coproduction biorefinery. The energy demands restricted production rates of both ethanol and

furfural as the feedstock to the biorefinery was driven by feedstock bypass requirements needed to supply energy to both the biorefinery and sugar mill. The two-stage furfural and ethanol co-production biorefinery was more capital intensive than the one-stage furfural and ethanol co-production biorefinery, but higher ethanol productivity led to lower MESPs than the one-stage furfural and ethanol co-production biorefinery. The two-stage furfural and ethanol co-production biorefinery utilising medium severity pretreatment was more robust as its profitability was less affected by fluctuations in product prices. Life cycle assessment studies are needed to provide more information on the environmental impact caused by each of the biorefinery configurations.

#### Acknowledgements

We thank National Research Fund (South Africa) and Sugar Milling Research Institute for financial and technical support. The Sugarcane Technology Enabling Programme for Bioenergy (STEP-Bio), a public: a private partnership between the South African sugarcane processing industry and the Department of Science and Technology (DST) Sector Innovation Fund (SIF) is acknowledged for partial financial support. The authors gratefully acknowledge Aspen Technology Inc. for provision of the Aspen Plus<sup>®</sup> academic licenses used to carry out this work, Aspen Plus<sup>®</sup> is a registered trademark of Aspen Technology Inc.

#### References

Avci, A., Saha, B.C., Kennedy, G.J., Cotta, M.A., 2013. High temperature dilute phosphoric acid pretreatment of corn stover for furfural and ethanol production. Ind. Crops Prod.

171

50, 478-484. https://doi.org/10.1016/j.indcrop.2013.07.055

- Bohre, A., Dutta, S., Saha, B., Abu-omar, M.M., 2015. Upgrading Furfurals to Drop-in
  Biofuels: An Overview. ACS Sustain. Chem. Eng. 3, 1263–1277.
  https://doi.org/10.1021/acssuschemeng.5b00271
- Cai, C.M., Zhang, T., Kumar, R., Wyman, C.E., 2014. Integrated furfural production as a renewable fuel and chemical platform from lignocellulosic biomass. J. Chem. Technol. Biotechnol. 89, 2–10. https://doi.org/10.1002/jctb.4168
- Cardona, C.A., Quintero, J.A., Paz, I.C., 2010. Production of bioethanol from sugarcane bagasse: Status and perspectives. Bioresour. Technol. 101, 4754–4766. https://doi.org/10.1016/j.biortech.2009.10.097
- Dashtban, M., Technologies, A., Dashtban, M., 2012. PRODUCTION OF FURFURAL: OVERVIEW AND CHALLENGES. J. Sci. Technol. For. Prod. Process. 2, 44–53.
- de Jong, W., Marcotullio, G., 2010. Overview of Biorefineries based on Co-Production of Furfural, Existing Concepts and Novel Developments. Int. J. Chem. React. Eng. 8, 1–24. https://doi.org/10.2202/1542-6580.2174
- Farzad, S., Mandegari, M.A., Guo, M., Haigh, K., Shah, N., Görgens, J.F., 2017. Multi-product biorefineries from lignocelluloses: A pathway to revitalisation of the Sugar Industry?
  Biotechnol. Biofuels 10, 1–24. https://doi.org/10.1186/s13068-017-0761-9
- Gebreyohannes, S., Neely, B.J., Gasem, K.A.M., 2014. One-parameter modified nonrandom two-liquid (NRTL) activity coefficient model. Fluid Phase Equilib. 379, 196–205. https://doi.org/10.1016/j.fluid.2014.07.027

Gubicza, K., Nieves, I.U., Sagues, W.J., Barta, Z., Shanmugam, K.T., Ingram, L.O., 2016.

Techno-economic analysis of ethanol production from sugarcane bagasse using a Liquefaction plus Simultaneous Saccharification and co-Fermentation process. Bioresour. Technol. 208, 42–48. https://doi.org/10.1016/j.biortech.2016.01.093

- Hernández, V., Romero-garcía, J.M., Dávila, J.A., Castro, E., Cardona, C.A., 2014. Technoeconomic and environmental assessment of an olive stone based biorefinery. Resour. Conserv. Recycl. 92, 145–150. https://doi.org/10.1016/j.resconrec.2014.09.008
- Himmel, M.E., Ruth, M.F., Wyman, C.E., 1999. Cellulase for commodity products from cellulosic biomass. Curr. Opin. Biotechnol. 10, 358–364. https://doi.org/10.1016/S0958-1669(99)80065-2
- Hossain, S., Theodoropoulos, C., Yousuf, A., 2019. Techno-economic evaluation of heat integrated second generation bioethanol and furfural coproduction. Biochem. Eng. J. 144, 89–103. https://doi.org/10.1016/j.bej.2019.01.017
- Hu, F., Jung, S., Ragauskas, A., 2012. Pseudo-lignin formation and its impact on enzymatic hydrolysis. Bioresour. Technol. 117, 7–12.
   https://doi.org/10.1016/j.biortech.2012.04.037
- Humbird, D., Davis, R., Tao, L., Kinchin, C., Hsu, D., Aden, A., 2011. Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol: Dilute-Acid Pretreatment and Enzymatic Hydrolysis of Corn Stover, National Renewable Energy Laboratory.
- Jin, E., Mendis, G.P., Sutherland, J.W., 2019. Integrated sustainability assessment for a bioenergy system: A system dynamics model of switchgrass for cellulosic ethanol production in the U. S. midwest. J. Clean. Prod. 234, 503–520.

https://doi.org/10.1016/j.jclepro.2019.06.205

- Kapanji, K.K., Haigh, K.F., Görgens, J.F., 2019. Techno-economic analysis of chemically catalysed lignocellulose biorefineries at a typical sugar mill : Sorbitol or glucaric acid and electricity. Bioresour. Technol. 289, 121635.
  https://doi.org/10.1016/j.biortech.2019.121635
- Liu, L., Chang, H. min, Jameel, H., Park, S., 2018. Furfural production from biomass pretreatment hydrolysate using vapor-releasing reactor system. Bioresour. Technol. 252, 165–171. https://doi.org/10.1016/j.biortech.2018.01.006
- Mandegari, M.A., Farzad, S., Görgens, J.F., 2017. Economic and environmental assessment of cellulosic ethanol production scenarios annexed to a typical sugar mill. Bioresour. Technol. 224, 314–326. https://doi.org/10.1016/j.biortech.2016.10.074
- Mesa, L., Morales, M., González, E., Cara, C., Romero, I., Castro, E., Mussatto, S.I., 2014.
  Restructuring the processes for furfural and xylose production from sugarcane bagasse in a biorefinery concept for ethanol production. Chem. Eng. Process. Process Intensif. 85, 196–202. https://doi.org/10.1016/j.cep.2014.07.012
- Metkar, P.S., Till, E.J., Corbin, D.R., Pereira, C.J., Hutchenson, K.W., Sengupta, S.K., 2015. furfural using solid acid catalysts †. Green Chem. 17, 1453–1466. https://doi.org/10.1039/c4gc01912a
- Mokomele, T., Sousa, C., Balan, V., Rensburg, E. Van, Dale, B.E., Görgens, J.F., 2018. Ethanol production potential from AFEX <sup>™</sup> and steam - exploded sugarcane residues for sugarcane biorefineries. Biotechnol. Biofuels 11, 1–21. https://doi.org/10.1186/s13068-018-1130-z

- Moncada, J., Cardona, C.A., Higuita, J.C., Vélez, J.J., López-Suarez, F.E., 2016. Wood residue (Pinus patula bark) as an alternative feedstock for producing ethanol and furfural in Colombia: Experimental, techno-economic and environmental assessments. Chem. Eng. Sci. 140, 309–318. https://doi.org/10.1016/j.ces.2015.10.027
- Neves, P. V, Pitarelo, A.P., Ramos, L.P., 2016. Production of cellulosic ethanol from sugarcane bagasse by steam explosion: Effect of extractives content, acid catalysis and different fermentation technologies. Bioresour. Technol. 208, 184–194. https://doi.org/10.1016/j.biortech.2016.02.085
- Nhien, L.C., Long, N.V.D., Kim, S., Lee, M., 2016. Design and optimization of intensified biorefinery process for furfural production through a systematic procedure. Biochem.
   Eng. J. 116, 166–175. https://doi.org/10.1016/j.bej.2016.04.002
- Nieder-Heitmann, M., Haigh, K.F., Görgens, J.F., 2018. Process design and economic analysis of a biore fi nery co-producing itaconic acid and electricity from sugarcane bagasse and trash lignocelluloses. Bioresour. Technol. 262, 159–168.

https://doi.org/10.1016/j.biortech.2018.04.075

- Ntimbani, R.N., Farzad, S., Görgens, J.F., 2021a. Furfural production from sugarcane bagasse along with co-production of ethanol from furfural residues. Biomass Convers. Biorefinery. https://doi.org/https://doi.org/10.1007/s13399-021-01313-3
- Ntimbani, R.N., Farzad, S., Johann, F.G., 2021b. Techno-economic assessment of one-stage furfural and cellulosic ethanol co-production from sugarcane bagasse and harvest residues feedstock mixture. Ind. Crop. Prod. 162.

https://doi.org/https://doi.org/10.1016/j.indcrop.2021.113272.

- Özüdoğru, H.M.R., Haigh, K.F., Görgens, J.F., 2019. Techno-economic analysis of product biorefineries utilizing sugarcane lignocelluloses : Xylitol , citric acid and glutamic acid scenarios annexed to sugar mills with electricity co-production. Ind. Crop. Prod. 133, 259–268. https://doi.org/10.1016/j.indcrop.2019.03.015
- Petersen, A.M., Haigh, K., Görgens, J.F., 2014. Techno-economics of integrating bioethanol production from spent sulfite liquor for reduction of greenhouse gas emissions from sulfite pulping mills. Biotechnol. Biofuels 7, 1–14. https://doi.org/10.1186/s13068-014-0169-8
- Prajapati, B.P., Jana, U.K., Suryawanshi, R.K., Kango, N., 2020. Sugarcane bagasse sacchari fi cation using Aspergillus tubingensis enzymatic cocktail for 2G bio-ethanol production. Renew. Energy 152, 653–663. https://doi.org/10.1016/j.renene.2020.01.063
- Rosales-Calderon, O., Arantes, V., 2019. A review on commercial- scale high-value products that can be produced alongside cellulosic ethanol. Biotechnol. Biofuels 12, 1–58. https://doi.org/10.1186/s13068-019-1529-1
- Shi, X., Zhao, B., Zhou, H., Tian, Y., Qiao, Y., Ji, B., 2019. Direct Saccharification and
  Fermentation for High Glucose and Ethanol Production from Non-Detoxified Furfural
  Residue Without Any Pretreatment. Energy Technol. Environ. Sci. 4, 7844–7850.
  https://doi.org/10.1002/slct.201901367
- Silva, J.F.L., Selicani, M.A., Junqueira, T.L., Klein, B.C., Vaz, S., Bonomi, A., 2017. Integrated furfural and first generation bioethanol production: Process simulation and technoeconomic analysis. Brazilian J. Chem. Eng. 34, 623–634. https://doi.org/10.1590/0104-6632.20170343s20150643

Smithers, J., 2014. Review of sugarcane trash recovery systems for energy cogeneration in South Africa. Renew. Sustain. Energy Rev. 32, 915–925. https://doi.org/10.1016/j.rser.2014.01.042

- Watanabe, K., Tachibana, S., Konishi, M., 2019. Modeling growth and fermentation inhibition during bioethanol production using component pro fi les obtained by performing comprehensive targeted and non-targeted analyses. Bioresour. Technol. 281, 260–268. https://doi.org/10.1016/j.biortech.2019.02.081
- Xing, R., Wei, Q., Huber, G.W., 2011. Production of furfural and carboxylic acids from waste aqueous hemicellulose solutions from the pulp and paper and cellulosic ethanol industries<sup>†</sup>. Energy Environ. Sci. 4, 2193–2205. https://doi.org/10.1039/c1ee01022k
- Yan, K., Wu, G., Lafleur, T., Jarvis, C., 2014. Production, properties and catalytic
   hydrogenation of furfural to fuel additives and value-added chemicals. Renew. Sustain.
   Energy Rev. 38, 663–676. https://doi.org/10.1016/j.rser.2014.07.003
- Yoo, C.G., Kuo, M., Kim, T.H., 2012. Ethanol and furfural production from corn stover using a hybrid fractionation process with zinc chloride and simultaneous saccharification and fermentation (SSF). Process Biochem. 47, 319–326. https://doi.org/10.1016/j.procbio.2011.11.018
- Zang, G., Shah, A., Wan, C., 2020. Techno-economic analysis of an integrated biore fi nery strategy based on one-pot biomass fractionation and furfural production. J. Clean. Prod. 260, 120837. https://doi.org/10.1016/j.jclepro.2020.120837
- Zeitsch, K.J.J., 2000. The chemistry and technology of furfural and its many by-products, Sugar Series Vol. 13, Elsevier, The Netherlands. https://doi.org/10.1016/S1385-

# 8947(00)00182-0

Zhao, X., Liu, D., 2019. Multi-products co-production improves the economic feasibility of cellulosic ethanol : A case of Formiline pretreatment-based biore fi ning. Appl. Energy 250, 229–244.

#### **Chapter 7: Conclusions and Recommendations**

#### 7.1 Summary of main findings from contributions of research

# 7.1.1 Contribution 1: One-stage furfural production followed by ethanol production from furfural solid residues

Furfural production (170-200°C, 0-2 wt.% H<sub>2</sub>SO<sub>4</sub>) and fermentation of the resulting residual solids without any washing step were studied to investigate effects of furfural conditions on ethanol production. Furfural yields achieved were 13 to 69%, with the highest yield of 69% (11.44 g/100g raw biomass) achieved at 170°C and 0.5 wt.% H<sub>2</sub>SO<sub>4</sub> (CSF=2.94). The yield of furfural increased with an increase in severity, but started to decrease above CSF of 2.94 due to dominance of furfural degradation reactions. Formation of organic acids during furfural production (acetic acid and formic acid) increased with an increase in severity of the furfural conditions as reported in literature.

There was a compromise of either furfural or ethanol in all the one-stage furfural production conditions studied, such that the furfural and ethanol could not be both maximised. Ethanol yields of up to 96% were achieved when fermenting furfural residues produced at 170°C and 0.5 wt.% H<sub>2</sub>SO<sub>4</sub>. However, due to cellulose degradation in presence of acid, the maximum amount of ethanol obtained (17.19-17.32 g/100g of raw biomass) was from furfural residues produced at 200°C without addition of acid, which differed from conditions (170°C, 0.5 wt.% H<sub>2</sub>SO<sub>4</sub>) that maximised furfural. In the studied range of furfural conditions, 170°C and 0.25 wt.% H<sub>2</sub>SO<sub>4</sub> were the most suitable operational parameters for furfural and ethanol production in a sequential biorefinery, resulting in furfural mass of 7.64g/100g of raw biomass and ethanol mass of 9.86-10.91g/100g of raw biomass.

# 7.1.2 Contribution 2: One-stage furfural production followed by ethanol production from furfural solid residues

Techno-economic analysis of biorefinery producing furfural and ethanol using the one-stage furfural process and SSF fermentation developed using data generated in experimental work conducted as part of Contribution 1 was carried out to provide insights of such a sequential biorefinery. The use of a solids steam jacket vapour releasing reactor reduced steam consumption by furfural reactor by more than half when compared to conventional furfural reactor. In turn, this allowed integration of ethanol co-production from residual biomass that would have been otherwise needed as boiler fuel.

The most profitable (IRR=12.78%) integrated one-stage furfural and ethanol biorefinery implemented 170°C and 0.5 wt.% H<sub>2</sub>SO<sub>4</sub> as furfural production conditions where furfural yield (69%, 11.44g/100g of raw biomass) was maximised. Employing conditions (200°C, without acid) suitable for maximising ethanol mass resulted in less favourable process economics (IRR=8.68%). Production of only ethanol (IRR=10.18%) from the hemicellulose and cellulose was less profitable than when co-produced with furfural. However, producing only furfural (IRR=12.92%) was more profitable when compared to integrated furfural and ethanol biorefinery.

The ethanol only biorefinery possessed the most potential to achieve the lowest minimum ethanol-selling price. The results showed that MESP of 0.83 and 1.13 US\$/L were required instead of 1.14 and 2.54 US\$/L in the most promising one-stage furfural and ethanol integrated biorefinery at IRR values of 15 and 20%. The potential of the integrated one-stage furfural and ethanol biorefinery was disadvantaged by cellulose degradation during furfural

180

production, which in turn caused overall mass of ethanol produced to be low. Moreover, the high energy demands of the one-stage furfural process negatively affected production rates and possibly profitability since high feedstock bypass (>50%) to the boiler for steam and electricity production were required. High feedstock bypass to the boiler meant that there was low amount feedstock available to the biorefinery for conversion into target bioproducts.

# 7.1.3 Contribution 3: Techno-economic aspects of one-stage furfural and ethanol coproduction versus two-stage furfural and ethanol co-production

Techno-economic aspects of the ethanol co-production integrated with the two-stage furfural and one-stage furfural in a biorefinery concept were compared to determine which process configuration has more potential to lower ethanol minimum selling price. Employing the two-stage furfural method with ethanol co-production resulted in lower energy demands compared to the one-stage furfural and ethanol co-production biorefinery as indicated by feedstock bypass requirements of 40% compared to 50%. The two-stage furfural and ethanol co-production biorefinery is the preferred configuration for improving ethanol economics as it achieved the lowest minimum ethanol selling price (0.73 US\$/L and 1.25 US\$/L) at 15 and 20% IRR, showing an improvement of 36-51% when compared to the most promising onestage furfural and ethanol co-production biorefinery. Increasing production by 25% lowered minimum ethanol selling price further to 0.51 and 0.99 US\$/L at 15 and 20% IRR demonstrating that the process benefits from economies of scale. Therefore, lowering feedstock bypass to the boiler will improve overall process economics and lower minimum ethanol selling price considering that the biorefinery was designed to be energy selfsufficient.

181

#### 7.2 Overall Conclusions

Amongst the two furfural and ethanol biorefinery configurations considered, the most promising two-stage furfural and ethanol integrated biorefinery has more economic potential (IRR=13.59%) than the most promising one-stage furfural and ethanol integrated biorefinery (IRR=12.78%). However, the two-stage furfural and ethanol integrated biorefinery required slightly higher capital investment (310 million US\$) than the one-stage furfural and ethanol integrated biorefinery (290 million US\$). Steam explosion pretreatment conditions (205°C and 13.5 min) employed in the two-stage furfural and ethanol co-production for production of xylose rich hydrolysate and enzymatically digestible solids, minimized cellulose degradation and consequently, the overall revenues were increased since the overall ethanol productivity increased. On the contrary, the one-stage furfural process is associated with cellulose degradation and lower ethanol yields from the residual biomass.

Furfural only biorefinery was associated with lower capital investments (259.5 million US\$) as the evaporation section to dewater residual biomass was not needed because furfural residual solid contained about 50% moisture and the ethanol production, purification and recovery sections were also not needed. However, without consideration of electricity by-products sales, the integrated one-stage furfural and ethanol biorefinery (IRR=10.30%) was more profitable than the furfural only biorefinery (IRR=9.91%), which shows less dependency on electricity sales. Noteworthy, the two-stage furfural and ethanol biorefinery remained the most profitable (IRR=11.78%) without electricity sales amongst the two integrated biorefinery strategies (one-stage furfural and ethanol or two-stage furfural and ethanol), primarily due to

improved productivity of ethanol and reduced feedstock bypass requirements for energy supply.

Ethanol production from the integrated two-stage furfural and ethanol biorefinery exploited the economic benefits from furfural co-product more than the ethanol production from the one-stage furfural and ethanol co-production biorefinery. The one-stage furfural and ethanol co-production biorefinery The one-stage furfural and ethanol co-production biorefinery suffered from low ethanol yields such that the required MESPs (1.14 US\$/L and 2.54 US\$/L) were higher than MESPs (0.73 US\$/L and 1.25 US\$/L) needed in the two-stage furfural and ethanol biorefinery to reach the same IRR values (15 and 20%).

Increasing production scale by 25% resulted in further improvements of ethanol economics since the MESPs were decreased in both the integrated biorefinery strategies considered (one-stage furfural and ethanol or two-stage furfural and ethanol). Therefore, process energy demands (steam and electricity), which were supplied from burning a portion of the feedstock in the boiler since the biorefineries were designed to be energy selfsufficient, limited realization of the economic potential of furfural and ethanol integration. Bypassing a portion of the feedstock to the boiler reduced the amount of biomass available for production of target products, which in turn negatively affected revenue needed for recovery of invested capital and turning a profit.

#### 7.3 Recommendations

#### 7.3.1 Optimisation of furfural residues fermentation and scale-up studies

Further investigation of the one-stage furfural production method and conditions as a way of minimising cellulose degradation and improving ethanol yields from the furfural residues is recommended. This can also assist in exploring ways of reducing energy consumption by the furfural process. Focus of further investigation should include optimisation of furfural solids loading, enzyme consumption and yeast inoculum requirements for fermentation of furfural residues. Reducing consumption of enzymes and yeast inoculum requirements will decrease operational costs, which are known to negatively affect process economics. Increasing solids loading of furfural residues during fermentation will increase ethanol concentrations and this will lower steam requirements by distillation used for ethanol purification and recovery. Scale-up studies of furfural and ethanol coproduction are also recommended to generate furfural and ethanol yield data that better reflects industrial scale operations. Scale-up studies will also help identify potential bottlenecks associated with furfural and ethanol co-production at a larger scale.

#### 7.3.2 Development of one-stage furfural reactor and furfural distillation optimisation

Profitability of the integrated one-stage furfural and ethanol co-production biorefinery were negatively affected by energy demands that were supplied by burning a portion of feedstock in the boiler. Therefore, an alternative one-stage furfural reactor that has lower energy consumption needs to be designed to ensure most of the feedstock is processed for furfural and ethanol production instead of being utilised as boiler fuel.

Furthermore, a detailed optimisation study of furfural separation by distillation should be conducted as a way of reducing steam consumption. Lower steam consumption result in less feedstock required by the boiler to provide for energy and this will in turn, increase feedstock available to the biorefinery. An alternative renewable energy source to supply for biorefinery and sugarmill energy demand is required to allow the biorefinery to realise its full economic potential.

# 7.3.3 Life cycle assessment and process flowsheet develop of the two-stage furfural process using reactive distillation as furfural reactor

Considering variation in properties of sugarcane bagasse and harvest residues (cane leaf matter), it is recommended that sequential furfural experiments followed by ethanol experiments be performed to determine actual discrepancies in product yield (furfural and ethanol) from experiments utilizing sugarcane bagasse only. Process intensification should be considered as a way of reducing capital investment costs and energy consumption. For example, furfural distillation can be intensified by replacing the two conventional columns with a bottom dividing wall column-decanter which is a single thermally coupled column as such a column has been reported to lower reboiler duty and is associated with lower operational costs. The two-stage furfural production process should consider employing a reactive distillation column to replace the furfural reactor as means of reducing capital and energy costs. It is also advisable to conduct Monte-Carlo simulations to give a better indication of product (furfural and ethanol) price fluctuations on the process profitability. Monte-Carlo simulations may also help determine impact of furfural price fluctuations on minimum ethanol selling price thereby indicating which biorefinery scenarios are more

185

robust. Lastly, life cycle assessment studies should be conducted to determine environmental impact of each biorefinery scenario. This will help assist in deciding which biorefinery is more sustainable and give an indication of how the overall biorefinery processes may be improved to reduce and/or prevent negative environmental impacts.

### Supplementary data for Chapter 4

Table S1-S4 present the analysis of variance (ANOVA) considering furfural reactor temperature and acid dosage as independent variables with response variables being furfural yield, ethanol yield, acetic and formic acid concentration.

	ANOVA; Var.:Furfural yield (g/100g); R-sqr=,94678; Adj:,88027 2 factors, 1 Blocks, 10 Runs; MS Pure Error=,0375251 DV: FF (g/100g)													
Factor	SS	df	MS	F	р									
(1)Temp (L)	15,96142	1	15,96142	425,3535	0,030844									
Temp (Q)	0,10478	1	0,10478	2,7924	0,343306									
(2)Acid (L)	5,29438	1	5,29438	141,0893	0,053470									
Acid (Q)	27,71131	1	27,71131	738,4747	0,023416									
1L by 2L	26,75937	1	26,75937	713,1066	0,023829									
Lack of Fit	4,23652	3	1,41217	37,6328	0,119128									
Pure Error	0,03753	1	0,03753											
Total SS	80,31583	9												

Table S1: ANOVA results for furfural yield (g/100g) as a response with acid and temperatures as factors.

Table S2: ANOVA results for ethanol yield (g/100g) as a response with acid and temperatures as factors

	ANOVA; Var.:Ethanol yield (g/100g); R-sqr=,90007; Adj:,77515 2 factors, 1 Blocks, 10 Runs; MS Pure Error=,0002748 DV: EtOH (g/100g)													
Factor	SS df MS F p													
(1)Temp (L)	0,9599	1	0,9599	3493,8	0,010769									
Temp (Q)	4,7565	1	4,7565	17312,1	0,004838									
(2)Acid (L)	228,8340	1	228,8340	832880,5	0,000698									
Acid (Q)	37,6766	1	37,6766	137130,6	0,001719									
1L by 2L	4,9626	1	4,9626	18062,1	0,004737									
Lack of Fit	31,4196	3	10,4732	38118,9	0,003765									
Pure Error	0,0003	1	0,0003											
Total SS	314,4117	9												

	ANOVA; Var.:Acetic (g/L); R-sqr=,83877; Adj:,63722 2 factors, 1 Blocks, 10 Runs; MS Pure Error=,0065539 DV: Acetic (g/L)													
Factor	SS	df	MS	F	р									
(1)Temp (L)	2,280899	1	2,280899	348,0242	0,034093									
Temp (Q)	0,163015	1	0,163015	24,8732	0,125978									
(2)Acid (L)	0,784013	1	0,784013	119,6263	0,058044									
Acid (Q)	0,380430	1	0,380430	58,0468	0,083084									
1L by 2L	3,337361	1	3,337361	509,2212	0,028193									
Lack of Fit	1,348002	3	0,449334	68,5603	0,088493									
Pure Error	0,006554	1	0,006554											
Total SS	8,401183	9												

#### Table S3: ANOVA results for acetic acid (g/L) as a response with acid and temperatures as factors

Table S4: ANOVA results for formic acid (g/L) as a response with acid and temperatures as factors

	ANOVA; Var.:Formic (g/L); R-sqr=,92528; Adj:,83187 2 factors, 1 Blocks, 10 Runs; MS Pure Error=,0011265 DV: Formic (g/L)													
Factor	SS	df	MS	F	р									
(1)Temp (L)	4,11056	1	4,11056	3648,83	0,010538									
Temp (Q)	3,48067	1	3,48067	3089,70	0,011452									
(2)Acid (L)	38,37797	1	38,37797	34067,05	0,003449									
Acid (Q)	3,05575	1	3,05575	2712,51	0,012222									
1L by 2L	1,11288	1	1,11288	987,88	0,020248									
Lack of Fit	4,15323	3	1,38441	1228,90	0,020966									
Pure Error	0,00113	1	0,00113											
Total SS	55,59711	9												



Figure S1: Profiles for predicted values and desirability considering acid dosage and temperature as independent factors with furfural yield and ethanol yield as response variables when using EthanolRed® (ER).

#### Appendix A



Figure S2: Profiles for predicted values and desirability considering acid dosage and temperature as independent factors with furfural yield and ethanol yield as response variables when using CelluX<sup>TM</sup>4 (C4).

### Supplementary data for Chapter 6

# Techno-economic assessment of two-stage furfural production and ethanol co-production from steam explosion pretreated lignocellulosic biomass

Rhulani N. Ntimbani, Somayeh Farzad\*, Johann F. Görgens

Department of Process Engineering, Stellenbosch University, Private Bag X1, Stellenbosch 7602, South Africa

Supplementary Data File contains 8 Figures that shows aspen screenshot of biorefineries

sections and 24 Tables summarising simulation results of Scenario 1-3.

\*Corresponding author. Tel.: +27 21 808 9485; fax: +27 21 808 2059. E-mail address: sfarzad@sun.ac.za

#### **List of Figures**

Figure S. 1: Steam explosion of feedstock and hydrolysate separation from pre-treated residua	al
solids	193
Figure S. 2: Furfural production, purification and recovery section	194
Figure S. 3: Bioethanol production by fermentation using Simultaneous Saccharification and	
fermentation technique	195
Figure S. 4: Ethanol purification using distillation columns and molecular adsorption sieves	196
Figure S. 5: Evaporation section for dewatering residual biomass from bioethanol section and	
concentrating residual sugars.	197
Figure S. 6: Biomass combustion area (boiler area) for production of steam and electricity	198
Figure S. 7: Water treatment section of the biorefinery	199
Figure S. 8: Condensing Extraction steam turbine unit used for extracting steam at various pre	ssure
and electricity	200

#### List of Tables

Table S. 1: Steam explosion Mass and energy simulation results for Scenario 1	201
Table S. 2: Steam explosion Mass and energy simulation results for Scenario 2	201
Table S. 3: Steam explosion Mass and energy simulation results for Scenario 3	201
Table S. 4: Furfural production, purification and recovery mass and energy simulation re	sults for
Scenario 1	202
Table S. 5: Furfural production, purification and recovery mass and energy simulation re	sults for
Scenario 2	

Table S. 6: Furfural production, purification and recovery mass and energy simulation results for
Scenario 3
Table S. 7: Bioethanol production mass and energy simulation results for Scenario 1           203
Table S. 8: Bioethanol production mass and energy simulation results for Scenario 2
Table S. 9: Bioethanol production mass and energy simulation results for Scenario 3         203
Table S. 10: Bioethanol purification and recovery mass and energy simulation results for Scenario 1
Table S. 11: Bioethanol purification and recovery mass and energy simulation results for Scenario 2
Table S. 12: Bioethanol purification and recovery mass and energy simulation results for Scenario 3
Table 5. 13: Evaporation section mass and energy simulation results for Scenario 1
Table S. 14: Evaporation section mass and energy simulation results for Scenario 2
Table S. 15: Evaporation section mass and energy simulation results for Scenario 3.         205
Table S. 16: Biomass combustion area mass and energy simulation results for Scenario 1.
Table S. 17: Biomass combustion area mass and energy simulation results for Scenario 2
Table S. 18: Biomass combustion area mass and energy simulation results for Scenario 3
Table S. 19: Water treatment section of the biorefinery mass and energy simulation results for
Scenario 1
Table S. 20: Water treatment section of the biorefinery mass and energy simulation results for
Scenario 2
Table S. 21: Water treatment section of the biorefinery mass and energy simulation results for
Scenario 3
Table S. 22: Condensing Extraction steam turbine section mass and energy simulation results for
Scenario 1
Table S. 23: Condensing Extraction steam turbine section mass and energy simulation results for
Scenario 2
Table S. 24: Condensing Extraction steam turbine section mass and energy simulation results for
Scenario 3



Figure S. 1: Steam explosion of feedstock and hydrolysate separation from pre-treated residual solids



Figure S. 2: Furfural production, purification and recovery section



Figure S. 3: Bioethanol production by fermentation using Simultaneous Saccharification and fermentation technique.



Figure S. 4: Ethanol purification using distillation columns and molecular adsorption sieves



Figure S. 5: Evaporation section for dewatering residual biomass from bioethanol section and concentrating residual sugars.



Figure S. 6: Biomass combustion area (boiler area) for production of steam and electricity.



Figure S. 7: Water treatment section of the biorefinery



Figure S. 8: Condensing Extraction steam turbine unit used for extracting steam at various pressure and electricity

	Units	S101	S102	S103	S104	S105	S105A	S106	S107
From		\$C-1	SEP101	SP101	SP101		B1	R 101	SEP101
То		SP101	\$C-6	\$C-7	R 101	B1	R 101	SEP101	\$C-3
Substream: ALL									
Mass Flow	KG/HR	113529	43102.95	40870.44	72658.56	11653.35	11653.35	84311.91	41208.96
Mass Enthalpy	CAL/SEC	-7.9E+07	-3.6E+07	-2.9E+07	-5.1E+07	-1E+07	-1E+07	-6.1E+07	-2.5E+07

Table S. 1: Steam explosion Mass and energy simulation results for Scenario 1

# Table S. 2: Steam explosion Mass and energy simulation results for Scenario 2

	Units	S101	S102	S103	S104	S105	S105A	S106	S107
From		\$C-1	SEP101	SP101	SP101		B1	R 101	SEP101
То		SP101	\$C-6	\$C-7	R 101 B1		R 101	SEP101	\$C-3
Substream: ALL									
Mass Flow	KG/HR	113529	33236.99	56764.5	56764.5	12486.67	12486.67	69251.17	36014.18
Mass Enthalpy	CAL/SEC	-7.9E+07	-2.9E+07	-4E+07	-4E+07	-1.1E+07	-1.1E+07	-5E+07	-2.1E+07

Table S. 3: Steam explosion Mass and energy simulation results for Scenario 3

	Units	S101	S102	S103	S104	S105	S105A	S106	S107
From		\$C-1	SEP101	SP101	SP101		B1	R 101	SEP101
То		SP101	\$C-6	\$C-7	R 101 B1		R 101	SEP101	\$C-3
Substream: ALL									
Mass Flow	KG/HR	113529	56798.93	34058.7	79470.3	20774.48	20774.48	100245	43445.85
Mass Enthalpy	CAL/SEC	-7.9E+07	-4.6E+07	-2.4E+07	-5.6E+07	-1.8E+07	-1.8E+07	-7.3E+07	-2.7E+07

	Units	S1	S202	S203	S203P	S204	S207	S207A	S208	S209	S210	S211	S212	S212A	\$213	S213A	S214	S215	S215A	S216	S217	S4	S5	S7
From		S-L-SEP	\$C-4	S-L-SEP	R 201	B1	B2	C201	C201	C201	MX101	B6	B3	B12	B4	DEC201	C203	HX203	C203	C202	C202	B1	B12	DEC201
То		B1	R 201	C201	S-L-SEP	\$C-41	C202	B2	MX101	\$C-5	B6	DEC201	B1	C201	C203	B4	MX101	\$C-2	B12	\$C-44	MX101	B12	HX203	B3
Substream: Al	L.																							
Mass Flow Mass	KG/HR	7800.106	43102.95	35302.84	43102.95	7800.106	7833.555	7833.555	25996.64	31897.24	34755.71	34755.71	30424.59	30424.59	4331.117	4331.117	1082.779	3248.338	3248.338	156.6711	7676.884 -	30424.59	3248.338	30424.59
Enthalpy	CAL/SEC	5119400	-3.6E+07	-2.9E+07	-3.6E+07	5247500	5905400	5905500	-2.1E+07	-3.1E+07	-2.7E+07	-3.1E+07	-3E+07	-3E+07	1180200	1180300	-738600	-444490	-395120	-109250	5796700	-3E+07	-419930	-3E+07

# Table S. 4: Furfural production, purification and recovery mass and energy simulation results for Scenario 1

# Table S. 5: Furfural production, purification and recovery mass and energy simulation results for Scenario 2

	Units	S1	S202	S203	S203P	S204	S207	S207A	S208	S209	S210	S211	S212	S212A	S213	S213A	S214	S215	S215A	S216	S217	S4	S5	S7
From		S-L-SEP	\$C-4	S-L-SEP	R 201	B1	B2	C201	C201	C201	MX101	B6	B3	B12	B4	DEC201	C203	HX203	C203	C202	C202	B1	B12	DEC201
То		B1	R 201	C201	S-L-SEP	\$C-41	C202	B2	MX101	\$C-5	B6	DEC201	B1	C201	C203	B4	MX101	\$C-2	B12	\$C-44	MX101	B12	HX203	B3
Substream: A	LL																							
Mass Flow Mass	KG/HR	5249.37	33236.99	27987.62	33236.99	5249.37	6700.642	6700.642	22095.9	24905.08	29640.39	29640.39	25714	25714	3926.384	3926.384	981.5961	2944.788	2944.788	134.0128	6566.63	25714	2944.788	25714
Enthalpy	CAL/SEC	3/3/200	-2.9E+07	-2.4E+07	-2.9E+07	3833300	-4997600	-4997700	-1./E+U/	-2.6E+07	-2.3E+07	-2.6E+07	-2.5E+07	-2.5E+07	-1068800	-1068800	-668260	-402870	-358110	-93448.1	4904700	-2.5E+07	-380610	-2.5E+07

# Table S. 6: Furfural production, purification and recovery mass and energy simulation results for Scenario 3

	Units	S1	S202	S203	S203P	S204	S207	\$207A	S208	S209	S210	S211	S212	S212A	S213	S213A	S214	S215	S215A	S216	S217	<b>S</b> 4	S5	S7
From		S-L-SEP	\$C-4	S-L-SEP	R 201	B1	B2	C201	C201	C201	MX101	B6	B3	B12	B4	DEC201	C203	HX203	C203	C202	C202	B1	B12	DEC201
То		B1	R 201	C201	S-L-SEP	\$C-41	C202	B2	MX101	\$C-5	B6	DEC201	B1	C201	C203	B4	MX101	\$C-2	B12	\$C-44	MX101	B12	HX203	B3
Substream: AL	L																							
Mass Flow Mass	KG/HR	14301.64 -	56798.93	42497.29	56798.93	14301.64	9123.578	9123.578	31709.58	40194.48	41359.07	41359.07	38530.36	38530.36	2828.714	2828.714	707.1784	2121.535	2121.535	182.4716	8941.107	38530.36	2121.535	38530.36
Enthalpy	CAL/SEC	8497200	-4.6E+07	-3.3E+07	-4.6E+07	8653400	7452200	7452300	-2.6E+07	-3.9E+07	-3.4E+07	-3.8E+07	-3.8E+07	-3.7E+07	-772760	-772810	-483880	-290440	-258200	-127240	7325300	-3.7E+07	-274400	-3.8E+07

	Units	S301	S302	S303	S304	S305	S306	S307	S308	S309	S310	S311	S312	S313	S314	S315	S316	S317	S322	S323
From		\$C-24	V301	HX301				MX301	R 301	FLSH101	FLSH101				MX302	R 302	FLSH302	FLSH302	\$C-43	HX303
То		V301	HX301	R 302	MX301	MX301	MX301	R 301	FLSH101		MX302	MX302	MX302	MX302	R 302	FLSH302	\$C-9	\$C-10	HX303	R 302
Substream: ALL																				
Mass Flow	KG/HR	41208.96	41208.96	41208.96	2200	850	500	3550	3550	529.7088	3020.291	109652	5116	500	118288	254315	6866.772	247448	94817.42	94817.42
Mass Enthalpy	CAL/SEC	-2.6E+07	-2.6E+07	-2.6E+07	-1663900	-393660	-403450	-2461000	-2482000	-307780	-2174200	-1.1E+08	-2369300	-403450	-1.2E+08	-2.2E+08	-4049000	-2.2E+08	-7.7E+07	-7.8E+07

# Table S. 7: Bioethanol production mass and energy simulation results for Scenario 1

# Table S. 8: Bioethanol production mass and energy simulation results for Scenario 2

	Units	S301	S302	S303	S304	S305	S306	S307	S308	\$309	S310	S311	S312	S313	S314	S315	S316	S317	\$322	S323
From		\$C-24	V301	HX301				MX301	R 301	FLSH101	FLSH101				MX302	R 302	FLSH302	FLSH302	\$C-43	HX303
То		V301	HX301	R 303	MX301	MX301	MX301	R 301	FLSH101		MX302	R 303	MX302	MX302	R 302	FLSH302	\$C-9	\$C-10	HX303	R 303
Substream: ALL																				
Mass Flow	KG/HR	36014.18	36014.18	36014.18	2200	850	500	3550	3550	529.7088	3020.291	109652	5116	500	8636.291	219279	7961.258	211318	109538	109538
Mass Enthalpy	CAL/SEC	-2.2E+07	-2.2E+07	-2.2E+07	-1663900	-393660	-403450	-2461000	-2482000	-307780	-2174200	-1.1E+08	-2369300	-403450	-4947000	-2.1E+08	-4693400	-2.1E+08	-1.1E+08	-1.1E+08

# Table S. 9: Bioethanol production mass and energy simulation results for Scenario 3

_	Units	S301	S302	S303	S304	S305	S306	S307	S308	S309	S310	S311	S312	S313	S314	S315	S316	S317	S322	S323
From		\$C-24	V301	HX301				MX301	R 301	FLSH101	FLSH101				MX302	R 302	FLSH302	FLSH302	\$C-43	HX303
То		V301	HX301	R 302	MX301	MX301	MX301	R 301	FLSH101		MX302	MX302	MX302	MX302	R 302	FLSH302	\$C-9	\$C-10	HX303	R 302
Substream: ALL																				
Mass Flow	KG/HR	43445.85	43445.85	43445.85	2200	850	500	3550	3550	529.7088	3020.291	109652	5116	500	118288	273786	7027.643	266759	112052	112052
Mass Enthalpy	CAL/SEC	-2.9E+07	-2.9E+07	-2.9E+07	-1663900	-393660	-403450	-2461000	-2482000	-307780	-2174200	-1.1E+08	-2369300	-403450	-1.2E+08	-2.3E+08	-4117200	-2.3E+08	-8.5E+07	-8.6E+07

# Table S. 10: Bioethanol purification and recovery mass and energy simulation results for Scenario 1

	Units	S401	S402	S403	S404	S405	S406	S407	S408	S409	S410	S411	S412	S413	S414	S415	S416	S417	S418	S419	S420	S421	S422	S6	S7
			COMP40																						
From		MX401	1	HX401		C401	C401	MX402	P401	B5	C402	C402	C402	C403	C403	HX403	SPLT401	SPLT401	HX404	HX405	P402	HX405	HX406	B5	\$C-11
		COMP40																							
То		1	HX401	C401	C401		MX402	P401	B5	C402	\$C-12	MX401	C403	\$C-13	HX403	SPLT401	HX404	HX405	HX405	P402	C403	HX406	\$C-16	\$C-18	B5
Substrear	n: ALL																								
Mass					10780.3	6893.61	11020.					267.437	14852.1	8604.17	8432.11	8432.11	2184.15	6247.95	2184.15	2184.15	2184.15	6247.95	6247.95	41208.9	41208.9
Flow	KG/HR	7134.21	7134.21	7134.21	1	9	9	258469	258469	258469	243404	4	5	3	3	3	8	5	8	8	8	5	5	6	6
	-			-				-	-	-	-														
Mass	CAL/SE			418610		-	-	2.3E+0	2.3E+0	2.3E+0	2.1E+0		-	-	-	-	-	-	-	-	-	-	-		
Enthalpy	C	-4200900	-4153800	0	-1.1E+07	4069100	1.1E+07	8	8	8	8	-151880	8938100	8038600	3147400	3121200	1062600	2058600	1275300	1257200	1257200	2076700	2489900	-2.6E+07	-2.5E+07

 Table S. 11: Bioethanol purification and recovery mass and energy simulation results for Scenario 2

	Units	S401	S402	S403	S404	S405	S406	S407	S408	S409	S410	S411	S412	S413	S414	S415	S416	S417	S418	S419	S420	S421	S422	S6	S7
			COMP40																						
From		MX401	1	HX401		C401	C401	MX402	P401	B5	C402	C402	C402	C403	C403	HX403	SPLT401	SPLT401	HX404	HX405	P402	HX405	HX406	B5	\$C-11
		COMP40																							
То		1	HX401	C401	C401		MX402	P401	B5	C402	\$C-12	MX401	C403	\$C-13	HX403	SPLT401	HX404	HX405	HX405	P402	C403	HX406	\$C-16	\$C-18	B5
Substream	: ALL																								
Mass				8216.84	12910.1	7862.66	13264.3					255.584	16950.4	10002.2	9359.58	9359.58	2411.53		2411.53	2411.53	2411.53			36014.1	36014.1
Flow	KG/HR	8216.842	8216.842	2	3	3	1	224582	224582	224582	207382	4	7	3	6	6	7	6948.05	7	7	7	6948.05	6948.05	8	8
								-	-	-	-							-				-	-		
Mass	CAL/SE			-		-		2.2E+0	2.2E+0	2.2E+0	2.1E+0			-	-	-	-	228950	-	-	-	230940	276900		
Enthalpy	С	-4838500	-4783400	4822900	-1.4E+07	4637700	-1.4E+07	8	8	8	8	-145170	-1E+07	9313000	3485100	3455900	1166500	0	1400200	1380200	1380200	0	0	-2.2E+07	-2.1E+07

Table S. 12: Bioethanol purification and recovery mass and energy simulation results for Scenario 3

	Units	S401	S402	S403	S404	S405	S406	S407	S408	S409	S410	S411	S412	S413	S414	S415	S416	S417	S418	S419	S420	S421	S422	S6	S7
			COMP40																						
From		MX401	1	HX401		C401	C401	MX402	P401	B5	C402	C402	C402	C403	C403	HX403	SPLT401	SPLT401	HX404	HX405	P402	HX405	HX406	B5	\$C-11
		COMP40																							
То		1	HX401	C401	C401		MX402	P401	B5	C402	\$C-12	MX401	C403	\$C-13	HX403	SPLT401	HX404	HX405	HX405	P402	C403	HX406	\$C-16	\$C-18	B5
Substream:	ALL																								
				7298.02	11028.2	7056.54	11269.7					270.381	16410.1	9298.39	9597.76	9597.76	2486.00	7111.75	2486.00	2486.00	2486.00	7111.75	7111.75	43445.8	43445.8
Mass Flow	KG/HR	7298.024	7298.024	4	7	5	5	278041	278041	278041	261361	6	8	3	1	1	2	9	2	2	2	9	9	5	5
								-	-	-	-														
Mass	CAL/SE			-		-		2.4E+0	2.4E+0	2.4E+0	2.2E+0			-	-	-	-	-	-	-	-	-	-		
Enthalpy	С	-4271100	-4222800	4255900	-1.2E+07	4138400	-1.2E+07	8	8	8	8	-153840	-1E+07	9160000	3582500	3552600	1209400	2343200	1451500	1430900	1430800	2363800	2834100	-2.9E+07	-2.7E+07
Table S. 13: Evaporation section mass and energy simulation results for Scenario 1.

			S204																									
	Units	S1	А	S501	S502	S503	S504	S505	S506	S507	S508	S509	S510	S511	S512	S513	S514	S515	S516	S517	S518	S519	S520	S521	S522	S523	S524	S525
		SPLT		\$C-	FLSH	FLSH				COM	FLSH	FLSH	SPLT		FLSH	FLSH	FLSH	FLSH	HX50	HX50	HX50	FLSH	MX5	\$C-	HX50	FLSH	HX5	
From		502	\$C-42	17	501	501	B2	B2		P501	502	502	502	B3	503	503	504	504	1	3	2	505	02	22	5	505	04	P501
			FLSH	FLSH	HX50		SPLT	FLSH	COM	FLSH5			FLSH		HX50	FLSH	FLSH	HX50	MX5	MX5	MX5	MX5	HX5	HX50	\$C-			\$C-
То		B3	501	501	1	B2	502	502	P501	02		\$C-19	503	\$C-8	2	504	505	3	02	02	02	02	04	5	21	B3	P501	20
Substr	eam:																											
ALL																												
Mass	KG/	4452	7800.	2434	2784	2233	1781	4524	4778.	4778.	5802.	4422	1335	9481	2726	1063	7842	2789	2784	2789	2726	2813	1111			5028	1111	1111
Flow	HR	7.47	106	04	5.74	58	10	8.26	6	6	655	4.21	82	7.42	4.81	18	0.36	7.23	5.74	7.23	4.81	0.41	38	8000	8000	9.95	38	38
Mass		-	-	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Enth	CAL/	4.1E+	5247	2.1E	2.4E+	1.9E	1.6E	3.2E+	74.85	11437	8858	3.1E+	1.2E	7.7E+	2.4E+	9.4E	6.6E+	2.5E+	2.9E+	2.9E+	2.8E+	2.5E+	1.1E	6806	8224	3.7E+	1.1E	1.1E
alpy	SEC	07	500	+08	07	+08	+08	07	69	7	30	07	+08	07	07	+07	07	07	07	07	07	07	+08	500	800	07	+08	+08

Table S. 14: Evaporation section mass and energy simulation results for Scenario 2.

	Unit		S204	S318																				S52					
	S	S1	А	А	S501	S502	S503	S504	S505	S506	S507	S508	S509	S510	S511	S512	S513	S514	S515	S516	S517	S518	S519	0	S521	S522	S523	S524	S525
		SPLT	\$C-	\$C-	\$C-	FLSH	FLSH				COM	FLSH	FLSH	SPLT		FLSH	FLSH	FLSH	FLSH	HX50	HX5	HX5	FLSH	MX	\$C-	HX50	FLSH	HX5	P50
From		502	42	40	17	501	501	B2	B2		P501	502	502	502	B3	503	503	504	504	1	03	02	505	502	22	5	505	04	1
			FLSH	FLSH	FLSH	HX50		SPLT	FLSH	COM	FLSH5		\$C-	FLSH		HX5	FLSH	FLSH	HX5	MX5	MX5	MX5	MX5	HX5	HX50	\$C-		P50	\$C-
То		B3	501	501	501	1	B2	502	502	P501	02		19	503	\$C-8	02	504	505	03	02	02	02	02	04	5	21	B3	1	20
Substr	eam:																												
ALL																													
Mass	KG/	4705	5249	4456	2073	2610	2310	1882	4286	4778.	4778.	5819.	4181	1411	109	2557	1155	8924	2634	2610	263	255	2676	104			6248	104	104
Flow	HR	8.03	.37	1.8	82	0.36	92	32	0.27	6	6	484	9.39	74	538	5.9	98	9.88	8.3	0.36	48.3	75.9	9.83	794	7500	7500	0.05	794	794
Mass		-	-	-	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Enth	CAL/	4.7E+	3833	3.6E	2.1E	2.3E+	2.2E	1.9E	3.2E+	74.85	1143	9063	3.1E+	1.4E	1.1E	2.3E	1.1E	8.7E+	2.3E	2.7E+	2.7E	2.7E	2.4E+	1E+	6456	7808	6E+0	1.1E	1.1E
alpy	SEC	07	300	+07	+08	07	+08	+08	07	69	77	20	07	+08	+08	+07	+08	07	+07	07	+07	+07	07	08	000	200	7	+08	+08

Table S. 15: Evaporation section mass and energy simulation results for Scenario 3.

			S204																									
	Units	S1	А	S501	S502	S503	S504	S505	S506	S507	S508	S509	S510	S511	S512	S513	S514	S515	S516	S517	S518	S519	S520	S521	S522	S523	S524	S525
		SPLT5		\$C-	FLSH	FLSH				COMP	FLSH	FLSH	SPLT		FLSH	FLSH	FLSH	FLSH	HX50	HX50	HX50	FLSH	MX5	\$C-	HX50	FLSH	HX5	
From		02	\$C-42	17	501	501	B2	B2		501	502	502	502	B3	503	503	504	504	1	3	2	505	02	22	5	505	04	P501
			FLSH	FLSH	HX50		SPLT	FLSH	COMP	FLSH5			FLSH		HX50	FLSH	FLSH	HX50	MX50	MX50	MX50	MX50	HX5	HX50	\$C-			\$C-
То		B3	501	501	1	B2	502	502	501	02		\$C-19	503	\$C-8	2	504	505	3	2	2	2	2	04	5	21	B3	P501	20
Substr	eam:																											
ALL																												
Mass	KG/	4943	1430	2613	2867	2469	1977	4924	4778.	4778.	5816.	4820	1483	1120	2801	1202	9159	2869	2867	2869	2801	2897	1143			6261	1143	1143
Flow	HR	5.09	1.64	61	9.96	82	40	1.98	6	6	887	3.69	05	52	4.71	91	1.76	8.79	9.96	8.79	4.71	4.88	68	8000	8000	6.88	68	68
Mass		-	-	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Enth	CAL/	4.3E+	8653	2.2E	2.5E+	2.1E	1.7E	3.4E+	74.85	11437	8961	3.3E+	1.3E	8.5E	2.5E+	1E+0	7.2E+	2.5E+	2.9E+	3E+0	2.9E+	2.5E+	1.1E	6802	8217	4.2E+	1.2E	1.2E
alpy	SEC	07	400	+08	07	+08	+08	07	69	7	70	07	+08	+07	07	8	07	07	07	7	07	07	+08	600	200	07	+08	+08

Table S. 16: Biomass combustion area mass and energy simulation results for Scenario 1.

	Units	S601	S602	S602A	S604	S606	S607	S608	S609	S610	S611	S612	S613	S614	S615
From		\$C-26		B1	\$C-25	FLSH601	FLSH601	MX601	COMP601	HX601	R 601	HX602	HX603	SPLT601	SPLT601
То		R 601	B1	COMP601	FLSH601		MX601	R 601	HX601	R 601	HX602	HX603	SPLT601		
Substrean	n: ALL														
Mass															
Flow	KG/HR	40870.44	12001.83	780119	44224.21	0	44224.21	44224.21	780119	780119	865214	865214	865214	861567	3646.601
Mass													-	-	-
Enthalpy	CAL/SEC	-2.9E+07	-139160	-9045300	-3.1E+07	0	-3.1E+07	-3.1E+07	-8962000	-775270	-6E+07	-1E+08	1.1E+08	1.1E+08	2191400

Table S. 17: Biomass combustion area mass and energy simulation results for Scenario 2.

	Units	S601	S602	S602A	S604	S606	S607	S608	S609	S610	S611	S612	S613	S614	S615
From		\$C-26		B1	\$C-25	FLSH601	FLSH601	MX601	COMP601	HX601	R 601	HX602	HX603	SPLT601	SPLT601
То		R 601	B1	COMP601	FLSH601		MX601	R 601	HX601	R 601	HX602	HX603	SPLT601		
Substrear	n: ALL														
Mass															
Flow	KG/HR	56764.5	12138.58	789007	41819.39	0	41819.39	41819.39	789007	789007	887591	887591	887591	883691	3900.783
Mass											-	-	-	-	-
Enthalpy	CAL/SEC	-4E+07	-140740	-9148300	-3.1E+07	0	-3.1E+07	-3.1E+07	-9064200	-585690	7.2E+07	1.1E+08	1.2E+08	1.2E+08	2279700

## Table S. 18: Biomass combustion area mass and energy simulation results for Scenario 3.

	Units	S601	S602	S602A	S604	S606	S607	S608	S609	S610	S611	S612	S613	S614	S615
From		\$C-26		B1	\$C-25	FLSH601	FLSH601	MX601	COMP601	HX601	R 601	HX602	HX603	SPLT601	SPLT601
То		R 601	B1	COMP601	FLSH601		MX601	R 601	HX601	R 601	HX602	HX603	SPLT601		
Substream	n: ALL														
Mass															
Flow	KG/HR	34058.7	11981.23	778780	48203.69	0	48203.69	48203.69	778780	778780	861043	861043	861043	857381	3662.124
Mass		-									-	-	-		-
Enthalpy	CAL/SEC	2.4E+07	-138920	-9029700	-3.3E+07	0	-3.3E+07	-3.3E+07	-8946700	-812130	5.7E+07	9.8E+07	1.1E+08	-1E+08	2195600

### Appendix B

Table S. 19: Water treatment section of the biorefinery mass and energy simulation results for Scenario 1.

	Unito	\$701	\$702	\$702	\$704	\$70E	\$706	\$707	\$709	\$700	\$710	6711	\$710	\$714	C71E	\$717	6710	\$710	\$720	\$721	5722	5772	5724	5725	5776	5777	\$779	\$720	\$720	C011
	UTIILS	3701	3702	3705	3704	3705	3700	3707	3706	3709	3710	3/11	3/12	3/14	3/15	3/1/	3/10	3/19	3720	3721	3722	3725	3724	3725	3720	3727	3720	3729	3730	3011
							SPLT70	SPLT70	SPLT7	SPLT70	MX70	FLSH7	FLSH7				SPLT7	SPLT7	FLSH7	FLSH7		MX70		FLSH7	FLSH7	FLSH7	FLSH7	MX70		
From		\$C-34			\$C-30	\$C-29	2	2	01	1	1	01	01	\$C-32	P701	\$C-33	03	03	02	02	P702	2	HX701	04	04	03	03	3-NA	HX702	\$C-47
		SPLT70	MX70	MX7		SPLT7			MX70	FLSH70	FLSH7		FLSH7	FLSH70	FLSH7	SPLT7	FLSH7	MX70		MX70		FLSH7	FLSH7				MX70			
То		1	1	01	MX701	02	MX701	MX702	1	2	01	P701	02	2	02	03	02	2	P702	2	HX701	03	04		\$C-27		3-NA	HX702		MX701
Substrea	am: ALL																													
Mass		31897.			8604.1	11113	18961.	92176.	12758.	19138.	13368	13368		1547.0	13368	10100			24526		24526	10227	24526		24540		11027	11027	11027	
Flow	KG/HR	24	90000	0	73	8	44	76	9	34	1	1	0	08	1	0	90900	10100	7	0	7	7	7	0	7	0	7	7	7	3200
Mass		-	-		-	-		-	-	-	-	-		-	-				-		-	-	-				-	-	-	-
Enthal	CAL/S	3.1E+0	9.3E+		803860	1.1E+0		9.5E+0	1.2E+0	1.9E+0	1.4E+0	1.4E+0		131620	1.4E+0	-		-	2.5E+0		2.5E+	1.1E+0	2.4E+0				1.1E+0	1.1E+	1.1E+	30869
ру	EC	7	07	0	0	8	-2E+07	7	7	7	8	8	0	0	8	1E+08	-9E+07	1E+07	8	0	08	8	8	0	-2E+08	0	8	08	08	00

 Table S. 20: Water treatment section of the biorefinery mass and energy simulation results for Scenario 2.

	Units	S701	S702	S703	S704	S705	S706	S707	S708	S709	S710	S711	S712	S714	S715	S717	S718	S719	S720	S721	S722	S723	S724	S725	S726	S727	S728	S729	S730	S811
							SPLT70	SPLT7	SPLT7	SPLT70	MX70	FLSH7	FLSH7				SPLT7	SPLT7	FLSH7	FLSH7		MX70		FLSH7	FLSH7	FLSH7	FLSH7	MX70		
From		\$C-34			\$C-30	\$C-29	2	02	01	1	1	01	01	\$C-32	P701	\$C-33	03	03	02	02	P702	2	HX701	04	04	03	03	3-NA	HX702	\$C-47
		SPLT70	MX70	MX7		SPLT7		MX70	MX70	FLSH70	FLSH7		FLSH7	FLSH70	FLSH7	SPLT7	FLSH7	MX70		MX70		FLSH7	FLSH7				MX70			
То		1	1	01	MX701	02	MX701	2	1	2	01	P701	02	2	02	03	02	2	P702	2	HX701	03	04		\$C-27		3-NA	HX702		MX701
Substrea Mass	am: ALL	24905.			10002.	10479	25528.	79265.	9962.0	14943.	13852	13852		3462.5	13852	10480			25125		25125	89745.	25125		25116		97245.	97245	97245	
Flow	KG/HR	08	90000	0	23	4	89	5	3	05	7	7	0	51	7	0	94320	10480	3	0	3	5	3	0	3	0	5	.5	.5	2900
Mass		-	-		-	-	-	-		-	-	-		-	-	-	-	-	-		-	-	-		-					-
Enthal	CAL/S	2.6E+0	9.3E+		931300	1.1E+0	2.7E+0	8.3E+0	-	1.5E+0	1.4E+0	1.4E+0		298050	1.4E+0	1.1E+0	9.5E+0	1.1E+0	2.6E+0		2.6E+	9.3E+0	2.5E+0		2.1E+0			-	-	26788
ру	EC	7	07	0	0	8	7	7	1E+07	7	8	8	0	0	8	8	7	7	8	0	08	7	8	0	8	0	-1E+08	1E+08	1E+08	00

## Table S. 21: Water treatment section of the biorefinery mass and energy simulation results for Scenario 3.

	Units	S701	S702	S703	S704	S705	S706	S707	S708	S709	S710	S711	S712	S714	S715	S717	S718	S719	S720	S721	S722	S723	S724	S725	S726	S727	S728	S729	S730	S811
From		\$C-34			\$C-30	\$C-29	SPLT70 2	SPLT70 2	SPLT70 1	SPLT70 1	MX70 1	FLSH7 01	FLSH7 01	\$C-32	P701	\$C-33	SPLT7 03	SPLT70 3	FLSH7 02	FLSH7 02	P702	MX70 2	HX701	FLSH7 04	FLSH7 04	FLSH7 03	FLSH7 03	MX70 3-NA	HX702	\$C-47
То		SPLT70 1	MX70 1	MX7 01	MX701	SPLT7 02	MX701	MX702	MX701	FLSH70 2	FLSH7 01	P701	FLSH7 02	FLSH70 2	FLSH7 02	SPLT7 03	FLSH7 02	MX702	P702	MX70 2	HX701	FLSH7 03	FLSH7 04		\$C-27		MX70 3-NA	HX702		MX701
Substre	am: ALL																													
Mass		40194.			9298.3	11436	18243.	96125.	16077.	24116.	13590	13590		973.47	13590				24424		24424	10537	24424		24437		11337	11337	11337	
Flow	KG/HR	48	90000	0	93	8	23	11	79	69	2	2	0	35	2	92500	83250	9250	2	0	2	5	2	0	4	0	5	5	5	2100
Mass		-	-		-	-	-	-	-	-	-	-			-	-	-	-	-		-	-	-				-	-	-	-
Enthal	CAL/S	3.9E+0	9.3E+		916000	1.2E+0	1.9E+0	9.9E+0	1.6E+0	2.3E+0	1.4E+0	1.4E+0		-	1.4E+0	9.2E+0	8.3E+0	91693	2.5E+0		2.5E+	1.1E+0	2.4E+0				1.2E+0	1.2E+	1.2E+	20689
ру	EC	7	07	0	0	8	7	7	7	7	8	8	0	827770	8	7	7	00	8	0	08	8	8	0	-2E+08	0	8	08	08	00

	Table S. 22: Con	densing Extraction	team turbine section mas	s and energy simu	lation results for Scenario 1
--	------------------	--------------------	--------------------------	-------------------	-------------------------------

	Units	S801	S802	S803	S804	S806	S809	S810	S811	S811A	S812	S813	S814	S816	S817	S818	S819	S820	S821	S822	S823	S824	S825	S826	S830
From		\$C-35	SPLT801	SPLT801	COMP801	SPLT802	SPLT802	COMP802	SPLT803	B3	SPLT804	SPLT803	COMP803	SPLT804	SPLT804	SPLT805	SPLT805	SPLT805	COMP804	HEAT801	HX801	MX801-N	IA	HX802	SPLT803
То		SPLT801		COMP801	SPLT802		COMP802	SPLT803	B3	\$C-46		COMP803	SPLT804	SPLT805	\$C-36	\$C-37	HX801	COMP804	HEAT801		MX801- NA	\$C-38	HX802	B1	
Substream	n: ALL																								
Mass Flow	KG/HR	245407	0	245407	245407	23500	221907	221907	3200	3200	0	207047	207047	199047	8000	1547.008	101000	96500	96500	96500	101000	101000	120792	120792	11660
Mass Enthalpy	CAL/SEC	-2E+08	0	-2E+08	-2.1E+08	-2E+07	-1.9E+08	-1.9E+08	- 2710000	- 3086900	0	-1.8E+08	-1.8E+08	- 1.7E+08	- 6806500	- 1316200	- 8.6E+07	-8.2E+07	-8.3E+07	-9.7E+07	-1E+08	-1E+08	- 1.2E+08	- 1.2E+08	- 9874600

# Table S. 23: Condensing Extraction steam turbine section mass and energy simulation results for Scenario 2

	Units	S801	S802	S803	S804	S806	S809	S810	S811	S811A	S812	S813	S814	S816	S817	S818	S819	S820	S821	S822	S823	S824	S825	S826	S830
From		\$C-35	SPLT801	SPLT801	COMP801	SPLT802	SPLT802	COMP802	SPLT803	B3	SPLT804	SPLT803	COMP803	SPLT804	SPLT804	SPLT805	SPLT805	SPLT805	COMP804	HEAT801	HX801	MX801-N	A	HX802	SPLT803
То		SPLT801		COMP801	SPLT802		COMP802	SPLT803	B3	\$C-46		COMP803	SPLT804	SPLT805	\$C-36	\$C-37	HX801	COMP804	HEAT801		MX801- NA	\$C-38	HX802	B1	
Substream	n: ALL																								
Mass Flow	KG/HR	251163	0	251163	251163	23500	227663	227663	2900	2900	0	212263	212263	204763	7500	3462.551	104800	96500	96500	96500	104800	104800	120792	120792	12500
Mass Enthalpy	CAL/SEC	- 2.1E+08	0	-2.1E+08	-2.1E+08	-2E+07	-1.9E+08	-2E+08	۔ 2484700	- 2678800	0	-1.8E+08	-1.8E+08	- 1.8E+08	- 6456000	- 2980500	-9E+07	-8.3E+07	-8.4E+07	-9.8E+07	- 1.1E+08	- 1.1E+08	- 1.2E+08	- 1.2E+08	- 1.1E+07

## Table S. 24: Condensing Extraction steam turbine section mass and energy simulation results for Scenario 3

	Units	S801	S802	S803	S804	S806	S809	S810	S811	S811A	S812	S813	S814	S816	S817	S818	S819	S820	S821	S822	S823	S824	S825	S826	S830
From		\$C-35	SPLT801	SPLT801	COMP801	SPLT802	SPLT802	COMP802	SPLT803	B3	SPLT804	SPLT803	COMP803	SPLT804	SPLT804	SPLT805	SPLT805	SPLT805	COMP804	HEAT801	HX801	MX801-N	IA	HX802	SPLT803
То		SPLT801		COMP801	SPLT802		COMP802	SPLT803	В3	\$C-46		COMP803	SPLT804	SPLT805	\$C-36	\$C-37	HX801	COMP804	HEAT801		MX801- NA	\$C-38	HX802	B1	
Substream	n: ALL																								
Mass Flow	KG/HR	244374	0	244374	244374	23500	220874	220874	2100	2100	0	197974	197974	189974	8000	973.4735	92500	96500	96500	96500	92500	92500	120792	120792	20800
Mass Enthalpy	CAL/SEC	-2E+08	0	-2E+08	-2E+08	-2E+07	-1.8E+08	-1.9E+08	- 1777400	- 2068900	0	-1.7E+08	-1.7E+08	- 1.6E+08	- 6802600	-827770	- 7.9E+07	-8.2E+07	-8.3E+07	-9.7E+07	- 9.2E+07	- 9.2E+07	- 1.2E+08	- 1.2E+08	- 1.8E+07