THE PRODUCTION OF BIOETHANOL AND BIOGAS FROM PAPER SLUDGE

by

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Thesis presented in partial fulfilment

of the requirements for the Degree

of

MASTER OF ENGINEERING

(CHEMICAL ENGINEERING)

in the Faculty of Engineering

at Stellenbosch University

Supervisor

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December 2017

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December 2017

Abstract

Recent interest into the production of biofuels such as bioethanol and biogas has increased due to a concern of global climatic change and the depletion of fossil fuels. Sustainable feedstock for the production of these biofuels need to be found. One such source is a waste stream from the pulp and paper industry. Paper sludge, emanating from the primary clarifier in the waste water treatment area of the paper mill, consists of high amounts of cellulose and water which makes it an ideal substrate for biological conversions, such as fermentation and anaerobic digestion. The extensive mechanical and chemical processing during paper making acts as a pre-treatment step by disrupting the biomass structure, making it amenable for enzymatic hydrolysis, the first stage of the biological conversion process. Another advantage is the continuous, localised supply of paper sludge.

Two possible biological conversion processes, fermentation and anaerobic digestion, were investigated for the energy yields and economic benefits. The feasibility of these processes has been proven at laboratory scale, with the working volume of experiments conducted in the range of 250 ml, however the scale up to pilot scale still needs to be investigated. The impact of compositional variability in paper sludge from different mills was investigated by comparing process yields from a tissue and printed recycling mill, corrugated recycling mill and virgin fibre pulping mill.

Ethanol production through simultaneous saccharification and fermentation was investigated in 20 L reactors, using commercially available enzymes and an industrial *Saccharomyces cerevisiae* strain. Tissue printed recycle paper sludge yielded a final ethanol concentration and conversion of 27.8 g/L and 70.6%, respectively at a solids loading and enzyme dosage of 33% (w/w) and 15 FPU/g dry substrate, respectively. Corrugated recycle paper sludge yielded an ethanol concentration of 39.4 g/L and a conversion of only 65.7%, with a solids loading and enzyme dosage of 27% (w/w) and 11 FPU/g dry substrate, respectively. Virgin pulp paper sludge had the highest ethanol concentration and conversion of 46.8 g/L and 87.4%, respectively at a solids loading and enzyme dosage of 18% (w/w) and 20 FPU/g dry substrate.

Anaerobic digestion for biogas production was tested in 30 L reactors, using mixed inoculum obtained from the waste water treatment facility of a brewery. The methane production for tissue printed recycle, corrugated recycle and virgin pulp paper sludge was 31.6, 54.4 and 37.2 L/kg paper sludge, respectively. The achievable solids loading for tissue printed recycle and corrugated recycle paper sludge was 10% (w/v), while virgin pulp paper sludge was 6% (w/v).

The conceptual biofuel plant design for the tissue and printing recycle mills, corrugated recycle mills and virgin pulp mills was based on average paper sludge production rates of 66, 10 and 36 dry tonnes/day respectively. A cash flow analysis was completed for each processing scenario as well as each paper sludge in order to determine what the minimum fuel selling price would be. For the fermentation process, the minimum ethanol selling price for viable investments were R8.34/L, R15.68/L and R5.47/L, respectively at a weighed cost of capital of 12% (real terms). The current market price for ethanol is R8.39/L, showing that virgin pulp paper sludge was the most viable for bioethanol production via fermentation. For the anaerobic digestion process, the minimum methane selling prices were R99.71/kg, R102.39/kg and R146.46/kg, respectively for tissue printed recycle paper sludge, corrugated recycle paper sludge and virgin pulp paper sludge. However, the current market price of methane is R27.26/kg, making the anaerobic digestion process unfeasible. This is due to the low methane yields achieved from paper sludge digestion as well as the high capital investment required to process large volumes of paper sludge.

This study proved the feasibility of value addition to paper sludge, which subsequently reduces the amount of waste sent to landfill and benefits the industry revenue with an additional energy stream. Future endeavours are aimed at further reduction of landfill volumes through the anaerobic digestion of the residues after fermentation.

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Chapter 1: Introduction

Paper sludge: potential, not problem

1.1 Background and motivation

The production of biofuels gained more traction due to the decrease in the availability of crude oil as well as the pressure to change to more environmentally friendly and renewable biofuels (Deenanath et al. 2012). Several waste streams from industrial biomass processing contain cellulose and can be considered for biofuel production, with one such stream being the paper waste sludge stream originating from the pulp and paper industry. The pulp and paper industry produces a substantial amount of waste water, rich in short fibres that have been rejected during the paper making process (Lever 2015; Fan et al. 2003). Severe restrictions on landfilling have been put in place to prevent ground water pollution and reduce greenhouse gas production, with these restrictions also being applied to paper sludge due to its high moisture content. Natural degradation of organic waste on landfilling sites are prone to release high amounts of uncaptured gasses into the atmosphere, mainly carbon dioxide and methane (Kamali & Khodaparast 2015).

Paper sludge (PS) has a high moisture content of approximately 50%, which makes it unsuitable for combustion or incineration, resulting in little or no energy benefit. However, the high cellulose and hemicellulose content makes the stream ideal for energy production via bioprocessing (Alekhina et al. 2015). The environmental benefits of biofuel production from water rich waste are ample: avoided landfilling and subsequent landfill emissions, avoided transportation costs and the reclamation of valuable process water (Bajpai 2015).

The pulp and paper industry is one of the sectors that utilise large amounts of cellulosic biomass as feedstock for their products. The biofuels of potential interest from paper sludge in this study are bioethanol and biogas, which could be used as energy source within the paper mill to alleviate the dependence on fossil based energy sources (Kamali & Khodaparast 2015).

1.2 Research questions and objectives

The research questions that need to be answered in this study are:

- How do the characteristics and composition of paper sludge affect the fermentation and anaerobic digestion capabilities at pilot scale (i.e. working volumes of between 10L and 20L)?
- What is the economic feasibility of producing bioethanol or biogas from paper sludge, using the pilot scale experimental data as input for the economic model?

The research objectives are to:

- Select and characterise paper sludge from mills that are representative of the various types of South African paper and pulp mills.
- Determine the bioethanol concentration and conversion yields from fed-batch simultaneous saccharification and fermentation (SSF) experiments based on optimal process conditions reported in previous studies.
- Determine the biogas production yields and methane content during anaerobic digestion of paper sludge.
- Construct an Aspen Plus simulation to determine the mass and energy balances for bioethanol and biogas plants.
- Determine the key economic indicators (minimum fuel selling price) by completing a full economic analysis on bioethanol and biogas production, including the required capital investment as well as a cash flow analysis on the two process scenarios.

The research questions will be answered in the coming chapters, along with the way the objectives were met. The first research question will be answered in Chapter 3, with the second question answered in Chapter 4.

Chapter 2: Literature Review

In the first section of the literature review, paper sludge as a waste product is described. This includes a study of the origins of paper sludge from within the pulp and paper mill, as well as its composition and intrinsic characteristics, which make it amenable for biochemical processing. The second section details the fundamentals of fermentation and process considerations specific to paper sludge. The third section describes the fundamentals of anaerobic digestion, with emphasis on the digestion of paper related products.

2.1 Paper sludge, waste product from the paper and pulp industry

2.1.1 The paper and pulp industry

The main processing paths during the paper making process are presented in Figure 2-1. The materials used during the production of pulp and paper range from raw virgin wood to recovered fibre from waste paper.

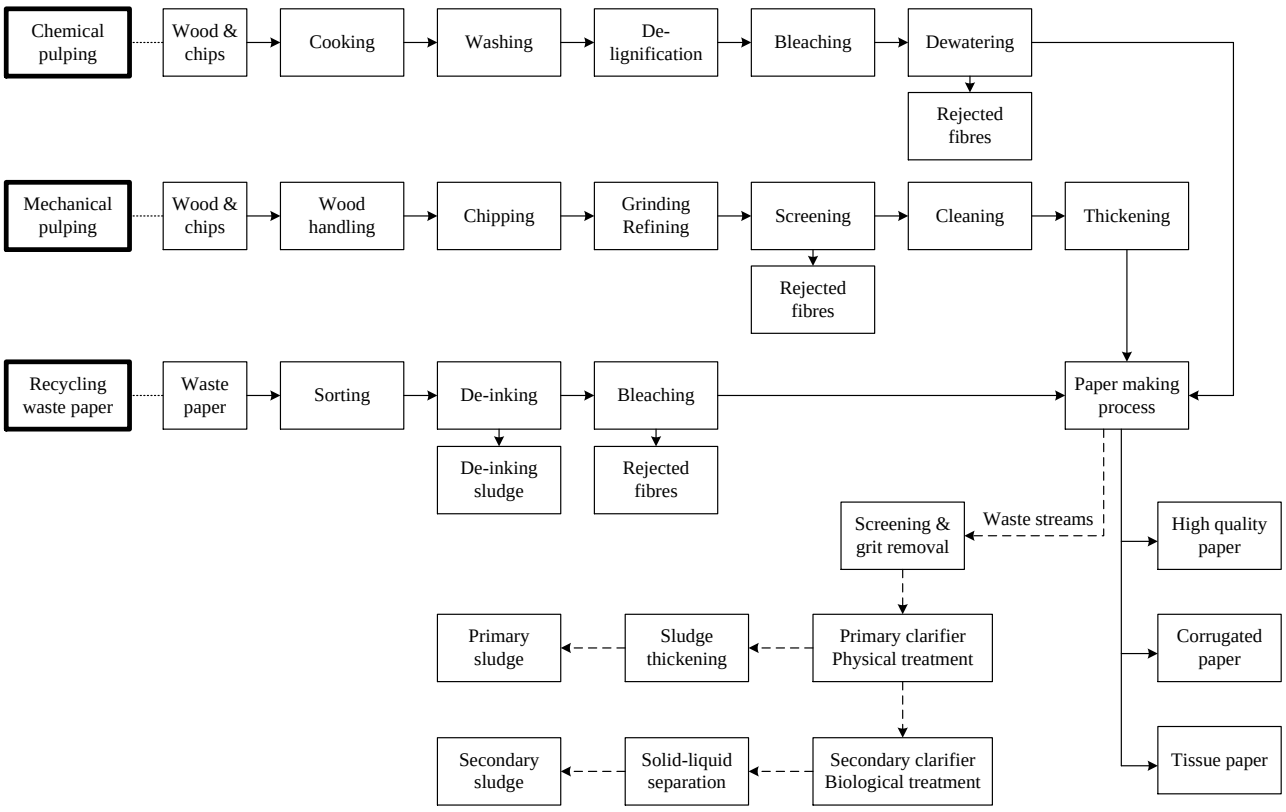

Figure 2-1: Paper pulping processes (Adapted from Gottumukkala et al. (2016))

Short fibres and fines are rejected at various locations within the mill and are treated in the primary clarifier section of the waste water treatment area. The sludge from the primary clarifier is then thickened through mechanical pressing and the final by-product is paper sludge.

2.1.1.1 Pulping of virgin fibre feedstock

Pulping refers to the process whereby wood material is reduced to individual fibres and starts with the removal of unwanted components of the raw wood feedstock such as soil, dirt and bark. The wood is then reduced in size, forming wood chips that are either chemically or mechanically digested ("cooked") at high temperatures and high pressures. The addition of digestion chemicals results in the removal via solubilisation of large amounts of lignin and hemicellulose, leaving pulp that consists primarily of cellulose (Bajpai 2015).

Various pulping methods include mechanical pulping, chemical pulping, thermo-mechanical pulping, chemo-mechanical pulping, and chemical thermo-mechanical pulping (Kamali & Khodaparast 2015). Mechanical pulping is often done with little or no addition of chemicals, thus resulting in a pulp that retains the majority of lignin and hemicelluloses in the raw material, together with cellulose. Mechanical pulping therefore typically delivers a higher pulp yield than chemical pulping, although the quality, or purity, of the final product is much lower. Further studies have found that pre-processing the raw material with chemicals before mechanical pulping (chemo-mechanical pulping) increases the process efficiency (Pokhrel & Viraraghavan 2004).

The Kraft process is a widely used form of chemical pulping. This alkaline process involves cooking the wood chips in a solution of sodium hydroxide and sodium sulphide, called white liquor, to remove the majority of lignin and hemicelluloses (Sainlez & Heyen 2012). The liquid stream which is separated from the pulp product, is called black liquor and is usually concentrated and burnt in a recovery furnace to return the chemicals needed for the cooking process. The next step involves the bleaching of the brown pulp, which is done to improve the brightness and stability of the pulp. The bleached pulp is then sent through a washing step to remove the bleaching agent (Ali & Sreekrishnan 2001).

The paper making stage is the final step in the manufacturing process. The processed pulp is combined with materials such as dyes, resins, sizing agents and fillers. Sizing agents include rosin and starch, while fillers are typically clays, titanium dioxide and calcium carbonate. The combination of these materials forms the paper web. This mixture is then sent to a press to remove the water, which results in paper sheets that need to be dried (Santos & Almada-Lobo 2012). Many studies are focussing on increasing the amount of fillers that can be added to the pulp, since fillers are generally

cheaper to produce than cellulose fibres. Fillers increase the smoothness and optical quality of the final paper product (Kamali & Khodaparast 2015). The end paper products produced from virgin wood is typically high quality paper (Gottumukkala et al. 2016)

2.1.1.2 Pulping of recovered fibre feedstock

The use of recovered fibre as feedstock for pulp production includes sources such as mixed office waste, old newsprint and old corrugated containers. The use of recovered fibre has the benefit of reducing the demand for virgin pulpwood, emissions and solid waste generation. Recovered fibre paper manufacturing involves three stages: pulping, high density screening and de-inking (Van Beukering & Bouman 2001).

The pulping stage involves dispersing the recycled fibres into water, while the screening stage removes foreign particles inherent to recycled material such as paper clips, staples, metals from ring binders and plastics. During the de-inking stage, the ink particles are removed from the cellulose fibres. The ink particles smaller than 25 µm are washed out, whereas the larger particles, usually toner inks and laser printed inks, can be removed through flotation where foam is collected on the top of flotation cells (Bajpai 2015). De-inking agents consist of chemicals such as hydrogen peroxide, sodium hydroxide and surfactants. The de-inking process increases the brightness of the pulp (Borchardt et al. 1998). Typical products from recovered fibre feedstock include tissue paper or corrugated paper (Gottumukkala et al. 2016).

2.1.2 Paper sludge

One of the main waste streams originating from pulp and paper mills, is the primary clarifier stream, which is comprised of short fibres, ash, fines and trace amounts of heavy metals. The papermaking process produces large amounts of waste water, which is treated by a conventional primary-secondary water treatment system (Monte et al. 2009). The screening of fibre produces fibre-rich water streams which are sent to the clarifiers, as shown in Figure 2-1.

Primary clarifier sludge originates from the primary waste water treatment unit of the pulp and paper mill, both for virgin and recycled fibre mills. The first stage of the waste water treatment removes suspended solids from the effluent via sedimentation in the primary clarifier and the solids are pressed to form the primary sludge (Mendes et al. 2014). Primary sludge (on a dry basis) is about 4% of the total paper product in virgin fibre mills and 15-30% in processed recycled fibre mills (Chen, Han, et al. 2014).

Secondary sludge emanates from the secondary treatment unit clarifier in the biological units of the waste water treatment section (Monte et al. 2009). The secondary clarifier from the aerobic activated sludge section produces smaller volumes of sludge since most of the heavy fibres have been removed in the primary clarifier (Coimbra et al. 2015). Secondary sludge is more difficult to process due to the high microbial content, for this reason only primary sludge will be considered for further processing (Gottumukkala et al. 2016).

2.1.2.1 Composition

Paper sludge consists of cellulose and hemicellulose which are two types of structural carbohydrates. The primary carbohydrate is cellulose which is a polymer with a rigid structure that is made up of repeating glucose units through hydrogen bonds. Cellulose is a highly stable polymer and is resistant to chemical attack (Gurram et al. 2015). The high amount of hydrogen bonding in the polymer aids in the rigidity of the cellulose structure (Bajpai 2015). Hemicellulose is the second predominant structural carbohydrate, which consists of a polymer made up of several short, branched sugars such as pentose sugars (xylose, arabinose) and hexose sugars (glucose, galactose and mannose). It is comparatively more amorphous and easy to breakdown due to branches in the hemicellulose structure (Guan et al. 2015).

Other components of paper sludge include lignin, ash and extractives. Lignin is a hydrophobic aromatic branched polymeric structure that is covalently linked to hemicellulose (Guan et al. 2015). It fills the space inside the cell walls between cellulose and hemicellulose, protecting the structural carbohydrates from degradation by microorganisms or enzymes (Yan et al. 2015). It is due to the recalcitrant nature of lignocellulose material, that pre-treatment steps are required to break the lignin seal and disrupt the crystalline structure of cellulose (Guan et al. 2015; Keller et al. 2003). Ash in paper sludge constitutes any inorganic matter, and is often found as calcium carbonate. Extractives are any materials found in the biomass that are not part of the cellular structure and include waxes, saps and fats (Sluiter et al. 2013).

Variability in sludge composition is due to the difference in the feedstock used and the type of operations carried out at the mill to treat the fibres (Monte et al. 2009). Various chemical compositions for paper sludge from South African mills are shown in Figure 2-2.

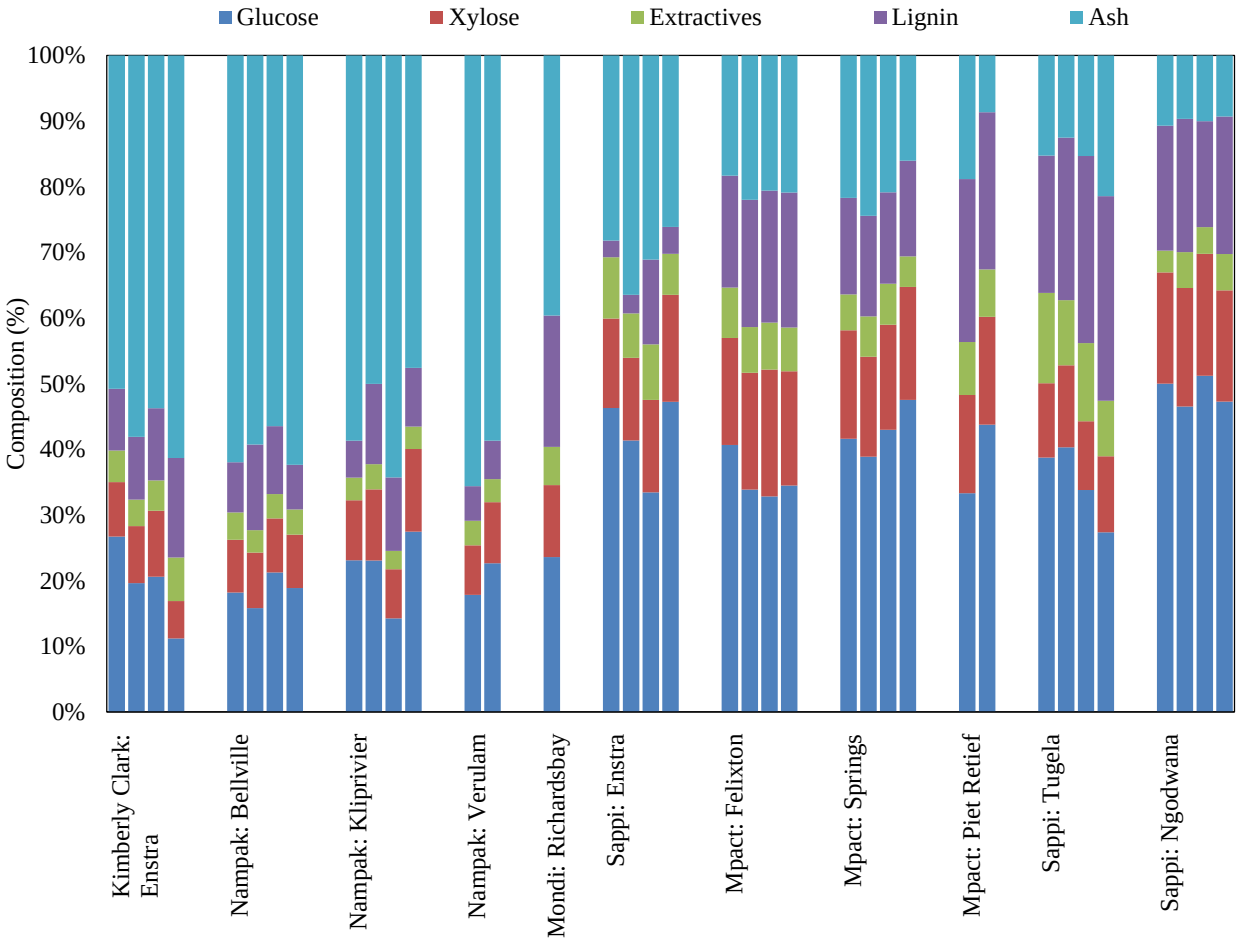

Figure 2-2: Chemical composition of paper sludge from South African paper & pulp mills (Adapted from Boshoff et al. (2016))

Paper sludge can be divided into three main categories, based on their composition as well as the feedstock used to produce the paper product. Boshoff et al. (2016) classified paper sludge from eleven mills as either tissue and printed recycle paper sludge (TPR-PS), corrugated recycle paper sludge (CR-PS) or virgin pulp paper sludge (VP-PS). Tissue printed recycle mills typically produce tissue paper from recycled fibre (newsprint, writing and printing paper) and virgin pulp. Corrugated recycle mills produce products such as containerboard, linerboard and coated board from recycled fibre and virgin pulp. Virgin pulp mills produce products such as dissolved pulp, mechanical pulp and chemical unbleached pulp from virgin wood (Eucalyptus or Pine). The composition of paper sludge varies significantly from mill to mill, and even within the same mill at different time intervals. Similar composition variance was reported by Fan & Lynd (2007a).

2.1.2.2 Current paper sludge disposal

Paper sludge that is not used in applications such as composting or brick making, is currently sent to landfill sites (Mendes et al. 2014). Prior to landfilling, paper sludge needs to undergo a form of conditioning, like thickening or dewatering, to an average moisture content of 50% (Boshoff et al. 2016). This is done to reduce the total volume of the sludge before being sent for disposal and to reclaim valuable process water, which also reduces the disposal cost. There are several processes for dewatering, which include centrifugation, band filters, filter presses and screw presses. Sludge with high levels of lignin are easier to dewater, since there is less cellulose present to retain the water (Monte et al. 2009).

Incineration of paper sludge is limited due to the high water and ash content of the paper sludge (Chen, Han, et al. 2014). At landfill sites, paper sludge starts to decompose and greenhouses gasses such as carbon dioxide and methane are released. The generation of these gasses and excessive amounts of acid and seepage of organic materials into the soil creates environmental problems. The treatment of paper sludge adds up to almost 60% of the total cost for waste water treatment at mills. Additional transportation costs are incurred if the landfill site is located far away from the mill (Monte et al. 2009). Municipal disposal areas are generally not equipped to handle wet sludge (Chen, Han, et al. 2014). Taking the above problems into account, alternative treatment methods need to be investigated.

Other uses include the conversion of paper sludge to valuable products (Reckamp et al. 2014, Ridout et al. 2016, Guan et al. 2016, Louw et al. 2016). These conversion methods are still being investigated for industrial application.

2.1.2.3 Advantages of using paper sludge for biochemical processing

There are several advantages in using paper sludge as feedstock for biological conversion through processes such as fermentation or anaerobic digestion.

No pre-treatment needed prior to fermentation and anaerobic digestion

One of the obstacles with the utilisation of lignocellulosic material as feedstock for the production of biofuels is the pre-treatment step. Cellulose, being inherently difficult to break down, and its association with lignin and hemicellulose, requires an additional pre-treatment step to disrupt its structure and make the residual carbohydrates accessible for enzymatic hydrolysis (Yan et al. 2015). The pre-treatment of lignocellulosic biomass aims to disrupt lignin and hemicellulose without the degradation of the sugars present in the biomass (Almeida et al. 2007). The pre-treatment step is often energy intensive and requires either a physical, chemical or thermal process (Lever 2015). Physicochemical technology such as microwave, ionising radiation, steam explosion, dilute acid, alkali and oxidation require high amounts of energy, whether as steam or as electricity. These pre-treatment methods require corrosion resistant, high pressure reactors, which increases the need for speciality equipment (Keller et al. 2003). Additionally, any pre-treatment via chemicals produce inhibitors that can be detrimental to the subsequent enzymatic hydrolysis and microbial fermentation. It also produces acidic or alkaline waste water which adds to the amount of waste water that needs to be cleaned up (Guan et al. 2015).

Paper sludge does not require such a pre-treatment step, since it has undergone several chemical, thermal or mechanical processes in the mill, such as pulping to liberate wood fibres, lignin removal, refining and bleaching. In comparison with raw wood, paper sludge fibres are more amenable to enzymatic hydrolysis (Chen, Han, et al. 2014; Fan et al. 2003).

Paper sludge from the Kraft process is more susceptible to enzymatic hydrolysis, since much of the lignin has been removed and cellulose fibres have been broken down during chemical processing, while processes like mechanical pulping leaves much of the lignin intact, which makes it more resistant to enzymatic hydrolysis (Lark et al. 1997).

Constant and localised supply of feedstock for bioprocessing

There is a reliable and stable supply of paper sludge available from mills (Wu et al. 2014). Paper sludge is produced at a permanent location, compared to other feedstock such as agricultural residues or wood sources that need to be obtained from various locations. Paper sludge is also supplied year round at constant rates (Chen, Han, et al. 2014). The process for conversion of paper sludge to energy products can also be integrated at an existing mill since most of the infrastructure already exists (Fan & Lynd 2007b) thus reducing both the transportation and processing costs (Hagelqvist 2013).

Land use and environmental impact

Around 5 million tonnes of paper sludge is discarded on landfill sites in Japan yearly (Prasetyo et al. 2011), while the United States produces 8 million tonnes and China around 12 million tonnes annually (Dwiarti et al. 2012). It is estimated that South Africa produces around 0.3 million tonnes of dry paper sludge annually, which is discarded on landfill sites (Boshoff et al. 2016). If the total amount of waste that needs to be disposed of can be reduced via biological treatment (fermentation and anaerobic digestion), the current load on land use can be reduced (Mendes et al. 2014). The use of paper sludge as material for biofuel production limits the amount of waste being sent to landfill. With a decreased amount of landfilling comes a decrease in the amount of greenhouse gas emissions (Chen, Han, et al. 2014; Dwiarti et al. 2012). Another environmental advantage is the replacement of fossil fuel energy, with "green" energy. Large amounts of water is also being landfilled with the paper sludge, while a biochemical process can retrieve much of this water and recycle it back into the mill (Bonilla et al. 2014).

2.1.2.4 Disadvantages for biochemical processes

Paper sludge emanating from paper mills that use recycled fibre have increased amounts of ash compared to paper sludge from virgin pulping processes, with amounts of up to 60% (w/w). The ash binds to the fibre and enzymes, which decreases the hydrolysis efficiency and increases the reactor size, which ultimately decreases the biofuel yield and increases production costs (Robus et al. 2016). Another disadvantage is the high water retention of the organic materials in paper sludge, which results in slurries with high viscosities that require energy intensive mixing. There is also very little free water available that negatively impacts the bioprocess, decreasing the bioethanol and biogas yields (Boshoff et al. 2016).

2.2 Fermentation

There are several process configurations for the production of ethanol, with the three most common being separate hydrolysis and fermentation (SHF), simultaneous saccharification and fermentation (SSF) and simultaneous saccharification and co-fermentation (SSCF).

Separate hydrolysis and fermentation

SHF occurs in two steps, the first is the hydrolysis of the carbohydrates to fermentable sugars, the second step is the fermentation of these sugars to ethanol (McMillan et al. 2011). The glucose produced during hydrolysis inhibits the β-glucosidase component in the cellulase enzyme cocktail. Cellobiose, an intermediate of glucose also largely reduces the reaction rate of cellulase components (Cantarella et al. 2004). The monomeric and dimeric sugars that inhibit the enzymes increases the production cost, since higher enzyme dosages would be required (Wu et al. 2014). SHF has the advantage of operating at separate optimal conditions for hydrolysis and fermentation (Wu et al. 2014). When these steps occur at different stages, there is an increase in utility and equipment costs, as well as an increase in operation time (Dwiarti et al. 2012).

Simultaneous saccharification and fermentation

SSF integrates the enzymatic hydrolysis of cellulose and the fermentation of the released glucose into one vessel, which significantly reduces equipment costs (Liu et al. 2015). This process has the advantage of reducing the inhibition of cellulase by avoiding the accumulation of sugar which occurs during SHF, since the sugar is utilised in fermentation concurrently with hydrolysis. This subsequently reduces the amount of cellulase required for hydrolysis, which eventually decreases the ethanol production cost (Wu et al. 2014). When hydrolysis and fermentation take place in a single vessel, the glucose that is formed is rapidly converted to ethanol by the yeast, which removes inhibitors from the broth (Cantarella et al. 2004). Product inhibition for cellulase starts to occur at glucose concentrations of 15 g/L (Kang et al. 2010). Ethanol productivity is high, since the glucose that is formed during saccharification can be fermented simultaneously (Hickert et al. 2013). The major drawback of this process is the difference in optimum operation conditions, such as temperature for hydrolysis and fermentation. Enzymatic hydrolysis typically has an optimal temperature of 50°C, whereas for fermentation, it is around 35°C (Kádár et al. 2004; Hasunuma & Kondo 2012). This can be overcome by using thermotolerant yeast strains, which has the added advantage of reducing the cooling costs of the fermenter and reducing the risk of bacterial contamination (Dwiarti et al. 2012).

Simultaneous saccharification and co-fermentation

SSCF is a similar process to SSF, however a yeast that is able to ferment both glucose and xylose is used. Primary paper sludge contains between 5 – 20% (w/w) xylose (Boshoff et al. 2016). A way to reduce the production cost of bioethanol is to increase the ethanol yield per ton of feedstock as well as the final ethanol concentration of the fermentation broth. This is facilitated through the co-fermentation of glucose and xylose (Erdei et al. 2013). To utilise all the sugar available, the hexose and pentose sugars released during hydrolysis needs to be fermented by a genetically engineered yeast strain (Sasaki et al. 2015). Wild type strains of *S. cerevisiae* and *Zymomonas mobilis* can only ferment hexose sugars, unless they have been genetically modified. Other yeasts such as *Pichia stipitis*, *Candida shehatae* and *Pachysolen tannophilus* have been used due to their ability to utilise xylose, however they have lower tolerance to inhibitors (Hickert et al. 2013).

The following biochemical reactions take place during the formation of ethanol by hydrolysis and fermentation (Guo et al. 2015). Equation (2-4) is only applicable to co-fermentation, where a xylose utilising yeast strain is used.

$$C_6H_{10}O_5 \ \ (cellulose) + H_2O \rightarrow C_6H_{12}O_6\ (glucose) \quad (2\text{-}1)$$

$$C_5H_8O_4 \ \ (hemicellulose) + H_2O \rightarrow C_5H_{10}O_5\ (xylose) \quad (2\text{-}2)$$

$$C_6H_{12}O_6 \rightarrow 2\ CH_3CH_2OH\ (ethanol) + 2\ CO_2 \quad (2\text{-}3)$$

$$3\ C_5H_{10}O_5 \rightarrow 5\ CH_3CH_2OH\ (ethanol) + 5\ CO_2 \quad (2\text{-}4)$$

2.2.1 Process conditions

2.2.1.1 Temperature

The optimal hydrolysis and enzyme temperature is around 50°C, while the optimal fermentation temperature is lower, ranging from 28°C to 37°C, depending on the strain of yeast that is used (Hasunuma & Kondo 2012). Mendes et al. (2014) carried out their SHF fermentation experiments at 50°C during hydrolysis and 30°C during fermentation. Fan et al. (2003) carried out their SSF experiments at 36°C. Robus et al. (2016) and Boshoff et al. (2016) operated their SSF experiments on various types of paper sludge at 37°C, which compromises between the optimum temperature for hydrolysis and fermentation.

2.2.1.2 Enzymes

The hydrolytic efficiency of cellulase cocktails has been the focus of several studies, with the focus having been switched from using only cellulase to the supplementation of cellulase with accessory enzymes to increase the enzymatic co-hydrolysis of the cellulose and hemicellulose (Van Dyk & Pletschke 2012). It has been found that these accessory enzymes increase the hydrolysis performance through synergistic benefits, without being directly involved in the hydrolysis of cellulose, thus boosting the release of fermentable sugars from the lignocellulosic biomass (Sun et al. 2015).

Cellulase enzyme preparations are enzyme cocktails consisting of endoglucanase, exoglucanase, β-glucosidase and small quantities of hemicellulase (Juturu & Wu 2014). Hemicellulase, or xylanase, hydrolyses the hemicellulose polysaccharide that coats the cellulose fibres, which boosts the hydrolysis of cellulose. Endoglucanase cleave the cellulose chains and reduce the degree of polymerisation, while exoglucanase removes cellobiose units from the ends of the cellulose chains. β-glucosidase hydrolyses cellobiose to glucose, decreasing the inhibitory effects of cellobiose on cellulase (Sun et al. 2015).

Components that occur naturally in lignocellulosic biomass exert significant restraints on the hydrolysis of cellulose. It has been found that lignin binds irreversibly to cellulase (Kadam et al. 2004; Lupoi et al. 2015), which is due to its inherent complexity and the hydrophobic nature of lignin (Xu et al. 2015). Since the lignin content of paper sludge can be anywhere in the range of 10 to 20% (w/w) (Boshoff et al. 2016), non-productive lignin binding can decrease the effectiveness of the cellulase and the sugars released.

From a techno-economic study conducted by Robus et al. (2016), it was found that the cost of enzymes contributed substantially to the production costs of ethanol. The enzymes thus impacted the economic viability of the process. It is therefore essential to keep the enzyme dosage as low as possible (Boshoff et al. 2016).

2.2.1.3 Yeast

S. cerevisiae is a yeast widely used in industrial ethanol production due to its high ethanol productivity, high yields and high resistance to ethanol inhibition. Additionally, *S. cerevisiae* is resistant to low pH, with an optimum growth range of between 5.0 and 5.5 (Park et al. 2010), as well as resistance to inhibitors derived from lignocellulosic biomass (Matsushika & Sawayama 2010). One drawback of *S. cerevisiae* is that it cannot naturally ferment xylose due to the lack of an active catabolic pathway for pentose sugars. A recombinant strain developed by Matsushika et al. (2009)

that can co-ferment glucose and xylose was engineered through chromosomal integration to express genes encoding xylose reductase and xylitol dehydrogenase from *P. stipitis*, along with the xylulokinase gene from a flocculent *S. cerevisiae* yeast, showing potential as a recombinant strain in large scale ethanol production using mixed sugar hydrolysate. Microorganisms that naturally ferment xylose include *P. stipitis* and *C. shehatae* (Mendes et al. 2014).

Fan et al. (2003) used *S. cerevisiae* D5A provided by the National Renewable Energy Laboratory (NREL) for the conversion of bleached Kraft paper sludge to ethanol. Semi-continuous SSF was carried out, achieving an ethanol yield of 0.47 g ethanol/ g glucose. Kádár et al. (2004) compared the ethanol yield of *Kluyveromyces marxianus* and *S. cerevisiae* using old corrugated cardboard and paper sludge as substrate, but found no observable difference. The ethanol yields for both strains ranged between 0.31 – 0.34 g ethanol/ g cellulose. Mendes et al. (2014) used *P. stipitis* DSM 3651 and *S. cerevisiae* as microorganisms for the fermentation of primary paper sludge with hydrochloric acid pre-treatment. *P. stipitis* performed better, with an ethanol yield of 0.39 g ethanol/g sugar compared to the *S. cerevisiae* yield of 0.33 g ethanol/g sugars.

Robus (2013) compared the ethanol production of two types of strains of *S. cerevisiae*. It was found that there was no significant difference in the level of ethanol production between MH1000 and D5A, although there was a distinct lag in fermentation activity during the first 24 hours for D5A. MH1000 is ethanol tolerant, but the fermentation of paper sludge does not yield ethanol concentrations that are high enough to reach the inhibition levels of 100 g/L ethanol. In a similar yeast screening study, Boshoff et al. (2016) screened *S. cerevisiae* strains MH1000, D5A and TMB3400. It was found that there was no significant difference in the final ethanol concentrations for various paper sludge types.

The presence of weak acids, such as acetic acid can inhibit yeast fermentations by decreasing the biomass formation by decreasing the cytosolic pH level which decreases the amount of adenosine triphosphate (ATP) that is available for biomass formation. As soon as cell growth stops, the ethanol production is also affected. Almeida et al. (2007) suggests that there are several mitigation strategies that can be applied. These include increasing the initial cell density in the fermentation broth which allows the yeast to naturally detox the broth or using a fed-batch operation mode which keeps the inhibitory compounds at low amounts.

2.2.1.4 Agitation and solids loading

One of the problems with using paper sludge as feedstock for ethanol production is the difficulty in the agitation of the viscous slurry. The paper sludge absorbs water resulting in a thick slurry that needs very high forces for agitation (Fan & Lynd 2007b). The density of the paper sludge and water mixture increases with an increase in solids loading. Increasing the solids loading also sharply increases the power requirements for mixing, due to the high viscosity of the broth (Fan et al. 2003).

A method generally applied to counter this problem is the use of fed-batch additions of paper sludge throughout the hydrolysis and fermentation process. As the hydrolysis proceeds, the cellulose is degraded, liberating more free water and reducing the viscosity of the broth. Elliston et al. (2013) reported that during the execution of fermentation experiments in a 10 L fermenter with high torque stirring capabilities, clumps of paper substrate often became trapped in the vessel which led to areas in the vessel that were not uniformly agitated. The solution was to lower the substrate loading. Cultures with lower solid loadings have more free water which reduces the viscosity of the slurry by increasing the lubricity of the particles. This reduces the power input necessary during mixing. Adequate mixing is required to ensure that there is sufficient contact between the enzymes and the substrate, as well as to ensure that there are no spots with increased amounts of hydrolysis and fermentation products which could inhibit the enzymes and yeast (Geng et al. 2015). At high lignocellulosic substrate concentrations, the solids effect comes in to play, where glucose yields become reduced as the substrate concentration is increased (Elliston et al. 2013). Water is the medium for enzymes to diffuse in and for products to diffuse away from reaction sites, and is therefore essential for hydrolysis (Geng et al. 2015).

High solids loadings are advantageous during fermentations, since the product concentrations increases, which increases the throughput of the plant and lowers the water and energy input. Capital and production cost are reduced due to the higher ethanol concentrations, since downstream processing operates more efficiently. As the solids loading increases, the enzyme dosage per unit of paper sludge also increases in order to maintain the hydrolysis performance, which increases the operating cost during fermentation (Martins et al. 2015).

2.2.1.5 Pelletisation and bulk density

Paper sludge received from pulp and paper mills in South Africa has a very heterogeneous particle shape and size, as well as a high moisture content and low energy density. This negatively affects its use as a solid biofuel (Castellano et al. 2015). However, pelletisation allows the paper sludge to be compacted to form high density, uniform solid biomass which can be used for different applications.

The quality of the pellets that are formed impact aspects such as the mechanical durability, bulk density and fine dust content (Castellano et al. 2015). The pelletisation process involves the extrusion of the material through a ring or flat hollowed die by the pressure of two or more rollers. The friction of the materials with the die channel increases the pressure and temperature, which causes the material to compress. The pellets are cut down to the required length by a blade once the material leaves the die channel. The agglomeration of the material is caused by an inter particle bonding mechanism due to the softening of different components at high pressures and temperatures (Castellano et al. 2015).

The bulk density is an indicator of the volume a certain mass of paper sludge will occupy. Taking into account parameters such as the bulk density, as well as the water holding capacity, one can get an idea of how the paper sludge will behave when water is added to it. Swelling, volume occupied, free water left, extent of possible agitation, all of these factors play a significant role on biochemical processing.

2.2.1.6 Water holding capacity

The water holding capacity of paper sludge depends on the amount of cellulose present and the length of the cellulose fibres, which contributes to the high viscosity of paper sludge (Boshoff et al. 2016). The water holding capacity of paper sludge can be decreased through fermentation, since the cellulose is converted to soluble sugars which are utilised by yeast to form ethanol. The water holding capacity of unfermented CR-PS was found to be 6.6 g water/ g paper sludge. After fermentation it was found to be 2.6 g water/ g paper sludge, which is a decrease of 61% (Boshoff et al. 2016). In a similar study, the water holding capacity of recycled paper sludge was found to decrease by 45% after fermentation with an enzyme dosage of 5 FPU/ g dry substrate (Lark et al. 1997).

2.2.1.7 Ash content

The ash content in paper sludge is mainly calcium carbonate, which causes the pH of the sludge to be neutral to alkaline (between 7 and 10). This pH is much higher than the optimal pH for fermentation (Chen, Han, et al. 2014). The ash content also limits the total fermentable solids loading capacity of the fermenter. The presence of high amounts of ash proportionally decreases the sugar content on a dry mass basis (Marques et al. 2008). The presence of calcium carbonate buffers the fermentation broth to near neutral, which has a significant impact on the cellulase activity, which is optimal at pH values of around 5 (Guan et al. 2016).

Chen et al. (2014) reported the mechanical fractionation of paper sludge via a two stage laboratory screen to remove ash. Primary sludge from the production of virgin and recycled products were used as feedstock. Mesh screens ranging from 100-mesh to 500-mesh were used with opening sizes

carrying between 0.152 mm to 0.025 mm. It was found that the fractionated sludge had an overall carbohydrate content of around 90% after the first stage. A fractionation barrier with a 400-mesh screen gave the highest fibre yield and highest ash removal ratios.

Guan et al. (2016) carried out similar ash removal to that of Kang et al. (2011), by first suspending the Kraft paper mill sludge in water, and then dewatering the slurry through a 100-mesh screen. The surface morphology of the paper sludge was also found to change after the de-ashing step. Scanning electron microscope (SEM) images showed that the washed sludge had a clean, smooth surface while the unwashed sludge had a rough surface with small particles visible on the surface. De-ashing also led to considerable loss of short fibres.

2.2.1.8 pH

The pH of the fermentation broth is important for both the enzymes and the yeasts. Acidic broths are classified as severe conditions and special strains of yeast are needed when the acidity of broths lies between a pH of 2 – 3 (Kodama et al. 2013). Most ethanologen microorganisms such as yeast have an optimum pH between 3 and 6 (Kang et al. 2010). Due to the presence of calcium carbonate in paper sludge fermentation broths, the pH stays between 4.8 and 5.5. This is due to the buffering effect of the calcium carbonate (Robus et al. 2016; Boshoff et al. 2016).

In a study on the enzymatic hydrolysis of Kraft paper mill sludge, it was found that the buffering action of ash kept the pH close to neutral, which was almost two units higher than the optimum required by the cellulase. However, during SSF runs it was noted that there was an improvement in the performance, which was attributed to a pH drop to around 5.5, caused by the production of carbonic acid and organic acids during fermentation. Low levels (less than 2.8 g/L) of lactic acid and acetic acid were identified in the fermentation broth, and it is suggested that these acids are not enough to dissolve all acid soluble ash, although they do interact with the calcium carbonate to form calcium acetate or calcium lactate buffers, which lower the pH (Kang et al. 2010).

2.2.2 Summary of fermentation of paper derived substrates

Several fermentation experiments have been conducted on paper sludge or similar paper derived products as feedstock, with varying solid loadings and enzyme dosages. Table 2-1 gives these values and the corresponding ethanol concentration and yields, which confirm the trends in key process parameters as described above.

Table 2-1: Ethanol production from paper sludge

Fermentation	Substrate	Substrate solid loading (g/L)	Cellulase (FPU/g dry substrate)	Ethanol concentration (g/L)	Conversion (%)	Reference
Batch	Recycled paper sludge	190	8	34	73	Lark et al. (1997)
	Recycled paper sludge	30	15	9	60	Kádár et al. (2004)
	Kraft paper sludge	135	34	26	75	Kang et al. (2010)
	Unspecified	170	10	40	89	Zhang & Lynd (2010)
	Primary sludge of virgin fibre	160	15	40	66.3	Prasetyo et al. (2011)
	Unspecified	5	15	11	80	Dwiarti et al. (2012)
	Kraft	135	22	23	66	Kang et al. (2011)
	De-ashed Kraft	139	16	24	71	Kang et al. (2011)
Fed-batch	De-ashed recycle	208	15	48	85	Robus et al. (2016)
	De-ashed recycle	218	14	57	94	Robus et al. (2016)
	Kraft paper sludge	180	20	34	67	Boshoff et al. (2016)
	Corrugated recycle	270	11	46	78	Boshoff et al. (2016)
Semi-continuous	Kraft paper sludge	195	24	50	74	Fan et al. (2003)
	Kraft paper sludge	130	32	42	92	Fan et al. (2003)

2.3 Anaerobic digestion

Biogas is produced via anaerobic digestion, a process that breaks down organic matter in the absence of oxygen. Biogas is composed of methane and carbon dioxide, with small amounts of hydrogen, ammonia and hydrogen sulphide (Meyer & Edwards 2014). In a review by Budzianowski (2016) on biogas as an interesting renewable and sustainable energy, it is mentioned that two factors are hindering its expansion as an economically viable energy technology: the high cost of digestible feedstock and the limited local availability of feedstock. Both these factors are overcome by using paper sludge as feedstock.

2.3.1 Reaction pathways

The anaerobic digestion process takes place in four stages: hydrolysis, acidogenesis, acetogenesis and methanogenesis (Karlsson 2010; Mao et al. 2015) with this intricate process shown in Figure 2-3. During hydrolysis, complex carbohydrates, proteins and lipids are broken down to glycerol, amino acids and fatty acids. In the acidogenesis stage, these products are broken down to form volatile fatty acids (propionate and butyrate), alcohols, hydrogen, carbon dioxide and ammonia. There is no build-up of sugars, since sugars are immediately converted from the hydrolysis stage to the acidogenesis stage (Labatut 2012). In the third stage (acetogenesis), the acids and alcohols are broken down to form hydrogen, carbon dioxide and acetic acid by hydrogen producing acetogenic bacteria and finally in the methanogenesis stage, acetic acid is broken down by methanogenic bacteria to form methane and carbon dioxide, and hydrogen and carbon dioxide are combined to form methane and oxygen. Some of the components, such as lignin, cannot be broken down and eventually form humus (Qi 2001). The stability of this process is dependent on the balance that exists between the bacteria in the digester (Angelidaki et al. 2009; Karlsson 2010).

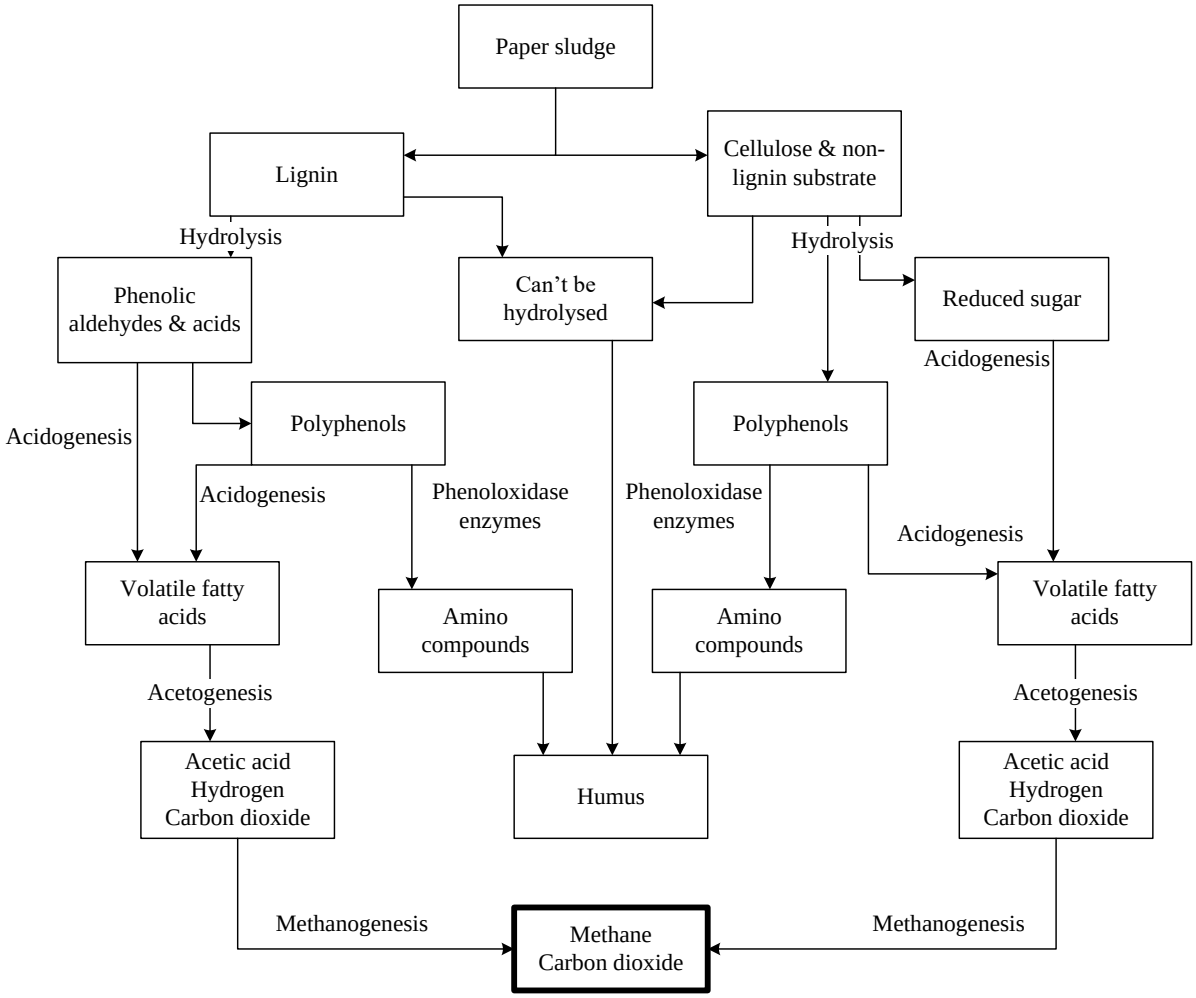

Figure 2-3: Anaerobic digestion pathway for paper sludge (Adapted from Qi (2001))

2.3.2 Process conditions

2.3.2.1 Temperature

The temperature influences the viscosity, surface tension and mass transfer properties of the substrate, while also affecting the activity of the microbial consortium that sustains the various process steps. Unstable temperatures cause a decrease in the biogas production. Anaerobic digestion rates and biogas yields are high when temperatures are in the range of 20°C to 60°C. Operation can therefore occur at either mesophilic (between 25°C and 40°C) or thermophilic (> 40°C) temperatures, depending on the consortium of microbes used for the conversion (Karlsson 2010). An increase in temperature has been found to increase the pH, the hydrolysis rate and the methane potential (Mao et al. 2015).

Thermophilic anaerobic digestion has faster reaction rates as well as higher load capacity, which results in higher productivities compared to mesophilic anaerobic digestion. However, acidification occurs at thermophilic temperatures, which can inhibit the biogas production. Other disadvantages include process instability, increased toxicity, larger investments, poor methanogenesis and a higher energy input (Mao et al. 2015). Temperatures exceeding 65°C can cause inhibition of the methanogen bioactivity. Mesophilic conditions show better process stability, but with slower degradation of the substrate and lower methane yields (Wieczorek et al. 2015). A decrease in temperature causes a decrease in the volatile fatty acid production rate, a decrease in the ammonia concentration and a decrease in the substrate utilisation rate, which decreases the final yields (Mao et al. 2015).

2.3.2.2 Agitation

The hydrolysis stage of anaerobic digestion depends on the hydrolytic enzymes excreted by the bacteria. In order to ensure adequate contact of these enzymes, proper mixing is required. Without proper mixing, hydrolysis will not occur and will severely inhibit the methane formation (Qi 2001). Biodigester systems that were built without agitation systems led to lower efficiencies as well as decreases in the biogas yield (Gutierrez et al. 2016). High solid loadings leads to very viscous slurries, which results in inefficient mixing and poor mass transfer that will cause a decrease in biogas production. In order to overcome these agitation limitation, a high-solids anaerobic digester was designed and consisted of three oblique impellers as well as a frame agitator, similar to an anchor impeller (Liao & Li 2015).

2.3.2.3 Retention time

Inherent to anaerobic digestion are slow biomass growth and substrate removal rates. In order to accommodate the slow microbial growth in anaerobic digestion, the sludge retention time needs to be longer than in aerobic digestion. Methanogenic bacteria need longer residence times to grow, in the range of 10 – 15 days. This is in contrast with the need for short hydraulic retention times, since large volumes of sludge needs to be treated quickly and economically. Another reason for long retention times is that the hydrolysis of organic matter causes a bottleneck in the digestion process, with complete hydrolysis of carbohydrates taking between 20 and 30 days. Retention time for complete digestion of complex, recalcitrant substrates such as lignocellulose and cellulose fibres is around 60 days. Longer retention time is coupled with larger reactors, and higher investment costs (Meyer & Edwards 2014).

2.3.2.4 pH

Optimal pH values for anaerobic digestion lie between 6 and 8.5. The production of carbon dioxide and volatile fatty acids affect the pH (Karlsson 2010). Excessive ammonium and nitrogen contents can inhibit the methanogenic activity and possibly cause the accumulation of volatile fatty acids. Total ammonium nitrogen causes inhibition at levels higher than 3000 mg/L. Methanogens that have acclimatised to high ammonia concentrations of 11 g/L should still be able to produce methane (Dalkılıc & Ugurlu 2015).

Certain products, listed in Table 2-2 are favoured at different pH values. At pH values of 5.2 – 6.3, hydrolysis and acidogenesis stages are at their optimum, while at a pH of 6.7 – 7.5, acetogenesis and methanogenesis area at their optimum pH (Serrano 2011).

Table 2-2: Anaerobic digestion pH favoured products (Serrano 2011)

pH	Favoured product
4.0 – 4.5	Propionate, ethanol
5.5	Acetate, propionate, butyrate, ethanol
6.0 – 6.5	Acetate, butyrate
8.0	Acetate, propionate

2.3.2.5 Carbon to nitrogen ratio

The optimum carbon to nitrogen ratio for anaerobic digestion feedstock lies in the range of 20:1 and 30:1. A lower C:N ratio can cause high volatile fatty acid accumulation or increase the total ammonia release, which will inhibit the digestion process. If this ratio is too low, nitrogen will be released and accumulated in the form of ammonium ions. Excessive concentrations of ammonium will increase the pH levels in the digester, which will have a toxic effect on the methanogen population (Montingelli et al. 2015). A higher C:N ratio will result in the rapid consumption of nitrogen by methanogens and lower the biogas yields (Kamali & Khodaparast 2015).

2.3.2.6 Inhibitors

Effluents such as paper sludge coming from the pulp and paper mill industry contain a large number of compounds. Among these compounds are several inhibitors, such as wood extractives, sulphur compounds and chlorinated compounds. In a study done on the digestibility of streams in Canadian pulp and paper mills, it was found that digestibility was higher in streams with no sulphur in the upstream process. The lowest digestibility was in streams containing bleaching effluents (Meyer & Edwards 2014).

Sulphur compounds, such as sulphate, sulphite, thiosulphate, sulphur dioxide and hydrogen sulphide are the most important inhibitors. Hydrogen sulphide is corrosive and adds to the chemical oxygen demand (COD) of the substrate. Methane yields are decreased since acetogenic bacteria and methanogenic archaea need to compete against sulphate reducing bacteria for the utilisation of volatile fatty acids (Montingelli et al. 2015). Sulphide concentrations higher than 100 mg/L may cause inhibition. Wood extractives such as resin acids, long chained fatty acids, volatile terpenes and tannins cause inhibitory effects (Meyer & Edwards 2014). Table 2-3 indicates the inhibitor and critical concentrations above which anaerobic inhibition has been reported.

Table 2-3: Anaerobic digestion inhibitors (Meyer & Edwards 2014)

Inhibitor	**Critical concentration (mg/L)**
Hydrogen sulphide	50-200
Sulphite	50
Sulphate	500
Resin acids	20-600
Fatty acids	70-1600
Volatile terpenes	40-330
Tannins	350-3000
Hydrogen peroxide	50

2.3.3 Summary of anaerobic digestion of paper derived substrates

Table 2-4 gives the results of previous batch studies done on biogas production from paper related wastes. There is very little literature available on the anaerobic digestion of primary sludge alone (Kamali & Khodaparast 2015). Co-digestion of primary and secondary paper mill sludge with municipal sewage sludge (Hagelqvist 2013), food waste (Lin et al. 2012) and monosodium glutamate waste liquor has been researched (Lin et al. 2011). The methane yields for various paper substrates varies from 45 L/kg volatile solids (VS) fed, to the highest of 370 L/kg VS obtained from office paper.

Table 2-4: Anaerobic digestion results for paper related substrates

Feedstock	**Methane yield (L/kg VS fed)**	**Methane yield (L/kg TS)**	**Reference**
Office paper	369	342	Gunaseelan (1997)
Corrugated card	278	272	Gunaseelan (1997)
Printed newspaper	100	98	Gunaseelan (1997)
Unprinted newspaper	84	82	Gunaseelan (1997)
Magazine	203	159	Gunaseelan (1997)
Primary sludge	45	-	Jokela et al. (1997)
Primary paper sludge	210	-	Bayr & Rintala (2012)
Secondary paper sludge	50	-	Bayr & Rintala (2012)
Secondary paper & pulp sludge	53	-	Hagelqvist (2013)
Secondary paper & pulp sludge	83	-	Huiliñir et al. (2014)
Activated paper & pulp sludge	170	-	Karlsson et al. (2011)

Chapter 3: Experimental study on the production of bioethanol and biogas from paper sludge

3.1 Introduction

The growth in the paper and pulp industry has resulted in an increased amount of solid waste, with the South African paper and pulp industry producing more than half a million tonnes of wet paper sludge (PS) every year (Boshoff et al. 2016). Waste valorisation offers an alternative to landfilling, with high value products and green energy acting as an incentive (Gottumukkala et al. 2016). Paper sludge emanates from the primary clarifier at paper mills, and has a moisture content varying between 50% and 80% by weight. Due to the high moisture content, biochemical processing routes are advantageous, since no energy intensive drying step is required (Boshoff et al. 2016).

This study aimed to show the effect of high solids loading and low enzyme dosages in fed-batch SSF for ethanol production. These values will be compared to those found in literature using equipment such as shake flasks, with smaller working volumes (100 ml opposed to 10 L). Furthermore, the study aimed to determine the methane yields that can be expected when anaerobic digestion is carried out in bioreactors under typical industrial conditions.

The experimental work conducted is not the optimisation of process conditions, but rather testing optimal conditions found in literature on a larger scale, in order to get an indication of yields and concentrations to be expected on pilot scale. These yields were used to develop simulation models and conduct economic evaluations, which are discussed in Chapter 4. The results were used to comment on the current state of technology available for paper sludge valorisation, and whether or not this waste stream can economically be converted to energy products. The key economic factors are critical for the implementation of these technologies at the paper and pulp mills.

3.2 Method and materials

3.2.1 Feedstock and characterisation

3.2.1.1 Feedstock preparation

Paper sludge samples were obtained from three different mills in South Africa, representing the three major paper and pulp mill operations, namely: tissue and printing recycling mills (Twincare Bellville), corrugated recycle paper mills (Mpact Felixton), and virgin pulp mills (Mondi Richards Bay). Tissue printed recycle paper sludge (TPR-PS), corrugated recycle paper sludge (CR-PS) and virgin pulp paper sludge (VP-PS) samples were dried in a hoop greenhouse at 40 - 45°C until dry. The dried paper sludge was subsampled using the cone & quarter method to ensure a homogenous mixture, after which the samples were milled using a hammer mill (Drotsky S1) fitted with a 2 mm screen. Paper sludge needed for fermentation experiments were pelletised (MPEL200, ABC Hansen Africa), to form compacted, high bulk density pellets with a 6 mm diameter. The milled and pelletised paper sludge was stored in sealed plastic bags at room temperature until needed.

Milled paper sludge was pelletised using a pellet mill (MPEL200, ABC Hansen Africa) with a die channel diameter of 6 mm. The pellet press specifications are given in Table 3-1. The dry, milled paper sludge was wetted with reverse osmosis water, in a paper sludge to water mass ratio of 2:1.

Table 3-1: Pellet press specifications

Property	**Value**
Die diameter (mm)	200
Die channel diameter (mm)	6
Engine power (kW)	7.5
Number of rollers (-)	2

3.2.1.2 Analytical methods

The chemical composition of all the samples was determined based on the National Renewable Energy Laboratory (NREL) standard procedures for biomass characterisation (Sluiter et al. 2008a; Sluiter et al. 2008b; Sluiter et al. 2012). The ash content was determined by placing crucibles in a muffle furnace at 575°C for four hours, after which the crucibles were placed in a desiccator for an hour and then weighed. This was repeated until a constant weight was achieved. A sample weighing between 0.5 – 2 g was then placed in a crucible and weighed. The sample was then ashed by being placed in the furnace for 24 hours. Crucibles were removed and placed in a desiccator to cool down and were then weighed until a constant weight was achieved. The oven dry weight and percentage ash can be calculated using Equations (3-1) and (3-2).

$$oven\ dry\ weight\ (ODW) = \frac{weight_{air\ dry\ sample} \times \%total\ solids}{100} \quad (3\text{-}1)$$

$$\%ash = \frac{weight_{crucible\ and\ ash} - weight_{crucible}}{ODW_{sample}} \times 100 \quad (3\text{-}2)$$

The extractives in the paper sludge sample were determined with a two-step extraction process to remove water soluble and ethanol soluble material. Ethanol extraction is required to remove interfering waxy materials that precipitate during the filtration of the acid hydrolysate in further analyses. A sample weighing between 2 - 10 g was added to a tared extraction thimble and inserted into the soxhlet tube. Water extractives were analysed using water in the tared receiving flasks, with reflux done for 6-24 hours. The ethanol extractives were tested by placing water in the ethanol receiving flask, with reflux taking place for 16-24 hours. The extracted solids were placed on filter paper in a Buchner funnel. The percentage extractives can be calculated using Equation (3-3).

$$\%extractives = \frac{weight_{flask\ and\ extractives} - weight_{flask}}{ODW_{sample}} \times 100 \quad (3\text{-}3)$$

Structural carbohydrates and lignin make up the bulk of paper sludge samples, and is determined by doing acid hydrolysis and subsequent analysis of the acid soluble and insoluble materials. The lignin fractionates into the acid soluble and acid insoluble material. The acid soluble lignin was measured by UV-Vis spectroscopy. The percentage acid insoluble residue (AIR), acid insoluble lignin (AIL), acid soluble lignin (ASL) and lignin is calculated using the equations below:

$$\%AIR = \frac{weight_{crucible\ and\ residue} - weight_{crucible}}{ODW_{sample}} \times 100 \quad (3\text{-}4)$$

$$\%AIL = \left(\frac{(weight_{crucible\ and\ residue} - weight_{crucible})}{ODW_{sample}} - \frac{(weight_{crucible\ and\ ash} - weight_{crucible})}{ODW_{sample}}\right) \times 100 \quad (3\text{-}5)$$

$$\%ASL = \frac{UV_{absorbance} \times volume_{hydrolysis\ liquor} \times dilution}{absorptivity(\epsilon) \times ODW_{sample} \times pathlength} \times 100 \quad (3\text{-}6)$$

$$dilution = \frac{volume_{sample} + volume_{diluting\ solvent}}{volume_{sample}}$$

$$\%lignin = (\%acid\ insoluble\ lignin + \%acid\ soluble\ lignin) \times \frac{100 - \%extractives}{100} \quad (3\text{-}7)$$

During the hydrolysis step, the polymeric carbohydrates are hydrolysed into monomers that are soluble in the hydrolysis liquid and were detected by high performance liquid chromatography (HPLC). Glucose, cellobiose, xylose, arabinose and ethanol concentrations were determined using an HPLC fitted with an Aminex HPx-8 column operated at 65°C and a Cation-H Micro-Guard cartridge. Analytes were eluted with 5 mM sulphuric acid at a flow rate of 0.6 ml/min. The area under the resulting peaks were related back to concentrations based on standards that are available commercially (Sigma-Aldrich). HPLC samples were analysed in duplicate per sample taken, with the average of the two values used.

The bulk density was determined by filling a 100 ml glass beaker with oven dried material at 105°C for 24 hours, using a method developed in house. The beaker was weighed before and after paper sludge samples were added, and the bulk density was determined using Equation (3-8).

$$Bulk\ density\ \left(\frac{kg}{m^3}\right) = \frac{dry\ paper\ sludge\ in\ beaker\ (kg)}{volume\ of\ beaker\ (m^3)} \quad (3\text{-}8)$$

The water holding capacity (WHC) was determined using a modified version of the method used by Boshoff et al. (2016). Paper sludge material was dried at 105°C for 24 hours. Approximately 1 g of paper sludge and 10 ml of water was placed in a 15 ml conical tube and vortexed to allow for proper mixing. The paper sludge was allowed to saturate at 20°C for 24 hours, after which the conical tubes were centrifuged at 2500 RCF (relative centrifugal force) and the supernatant decanted. The conical tube was weighed before and after, and the water holding capacity was determined using Equation (3-9).

$$WHC\ \left(\frac{L}{kg}\right) = \frac{wet\ paper\ sludge\ (kg) - dry\ paper\ sludge\ (kg)}{dry\ paper\ sludge\ (kg)} \times \rho_{water} \quad (3\text{-}9)$$

Gas compositional analysis was carried out using a fast biogas analyser (CompactGC 4.0, Global Analyser Solutions) equipped with three channels in order to measure carbon dioxide, methane, nitrogen and oxygen. The helium injection flow rate was set to a value of 5 ml/min for carbon dioxide detection, with the column oven at 50°C (Channel 2). The argon injection flow rate was set to 5 ml/min for methane, nitrogen and oxygen detection, with the column oven at 65°C (Channel 3). The gas samples were analysed in duplicate, with the standard deviation between duplicates being less than 2%.

Statistical analysis was completed using the Microsoft Excel built-in programme for single factor analysis of variance (ANOVA). The ANOVA was completed on the experimental ethanol concentration results (g/L) for the triplicate fermentation runs as well as the methane yield (L CH_4/kg PS) for the duplicate anaerobic digestion experiments.

3.2.2 Simultaneous saccharification and fermentation of paper sludge

Fed-batch SSF experiments were conducted in 20 L bioreactors (New Brunswick Scientific, Edison, N.J., U.S.A), with a final working mass of 10 kg. The reactors were fitted with three Rushton impellers and baffles to ensure efficient mixing.

An enzyme cocktail consisting of Viscamyl Flow (Danisco Genencor, Belgium) and Novozym 188 (Novozymes, Denmark) was used in a 10:1 volume ratio, with respective activities of 140 FPU/ml and 929 IU/ml, determined using the methods developed by Xiao et al. (2004) and Ghose (1987). An industrial strain of *S. cerevisiae* MH1000 was used, grown from glycerol freezer stocks kept at - 85°C. Yeast inoculum was grown in media containing 10 g/L yeast extract, 20 g/L peptone and 20 g/L glucose for 18 hours at 37°C and 150 RPM in an orbital shaker.

The reactors were loaded with reverse osmosis water, 3 g/L corn steep liquor, 0.62 g/L magnesium sulphate heptahydrate and the first 3% (w/w) paper sludge batch. The reactors were sterilised in-situ for 15 minutes at 121°C. The enzymes and yeast were then aseptically added to the reactors, with a yeast inoculation volume of 5% (v/v).

The enzyme dosage and final solids loading is shown in Table 3-2, based on optimal values (modified values) determined by Robus et al. (2016) and Boshoff et al. (2016). The reactors were run for 168 hours at 37°C and 500 RPM. Paper sludge feedings of 3% (w/w) were added every 12 hours, until the desired solids loading was achieved. Liquid samples of ~100 ml were taken every 24 hours for pH, sugar and ethanol determination.

Table 3-2: Enzyme dosage and solids loading for fermentation

Paper sludge	**Enzyme dosage (FPU/g dry substrate)**	**Enzyme dosage (FPU/g glucan)**	**Final solids loading (g/L)**
TPR-PS	15	72.2	330
CR-PS	11	29.3	270
VP-PS	20	38.4	180

The theoretical ethanol concentration and ethanol conversion was calculated using Equation (3-10) and Equation (3-11) which are based on the theoretical stoichiometric yields of 0.51 g/g for glucose and xylose.

$$Theoretical\ ethanol\ concentration\ \left(\frac{g}{L}\right) = solids\ fed\ \left(\frac{g}{L}\right) \times glucosefraction \times 0.51 \quad (3\text{-}10)$$

$$Ethanol\ conversion\ (\%) = \frac{experimental\ ethanol\ concentration\ \left(\frac{g}{L}\right)}{theoretical\ ethanol\ concentration\ \left(\frac{g}{L}\right)} \times 100 \quad (3\text{-}11)$$

The xylose conversion yield was calculated using Equation (3-12).

$$Xylose\ conversion\ \ (\%)\ = \frac{experimental\ xylose\ concentration\ \left(\frac{g}{L}\right)}{solids\ fed\ \left(\frac{g}{L}\right) \times xylosefraction\ \times 0.51} \times 100 \quad (3\text{-}12)$$

3.2.3 Anaerobic digestion of paper sludge

3.2.3.1 Inoculum preparation

Mesophilic inoculum was collected from the waste water treatment section of a brewery. The inoculum was allowed to settle and the supernatant decanted. The inoculum was incubated at 37°C and 93 RPM for two weeks to activate the microorganisms and to remove any residual substrate from the wastewater treatment section.

3.2.3.2 Batch digestion in 30 L vessel

Batch biogas experiments were conducted in 30 L digesters at 37°C and low speed mixing of 93 RPM for 28 days. The reactor has a shaft attached to a top driven motor, and is fitted with a single Rushton impeller at the bottom of the reactor. The digesters are jacketed vessels, with water circulating in the jacket. The reactor has a working volume of 21 L, which corresponds to 70% of the total volume. The total solids loading for TPR-PS and CR-PS was 10% (w/v), while VP-PS was 6% (w/v), based on previous unpublished studies conducted in house. The inoculum loading was 10% (w/w) of the total solids loading. Gas samples were collected from the upper part of the reactor and routed through a manometer-type online gas measurement system, with the gas volume calibrated based on the amount of displaced water in the manometer. Gas samples were collected in tedlar bags every 7 days for gas composition analysis in order to determine the methane content. Experiments were conducted in duplicate.

Table 3-3: Solids loading and inoculum loading for anaerobic digestion

Paper sludge	Solids loading (% w/v)	Inoculum loading (% w/w)
TPR-PS	10	10
CR-PS	10	10
VP-PS	6	10

3.3 Results and discussion

3.3.1 Characterisation of paper sludge

3.3.1.1 Chemical composition

The chemical composition for the three types of paper sludge is shown in Table 3-4. The composition is given for paper sludge as received from the mill.

Table 3-4: Chemical composition of various types of paper sludge

Paper sludge	Glucan (% w/w)	Xylan (% w/w)	Lignin (% w/w)	Extractives (% w/w)	Ash (% w/w)
TPR-PS	20.8 ± 0.1	4.9 ± 0.2	6.4 ± 0.1	5.1 ± 0.1	62.9 ± 0.4
CR-PS	37.5 ± 0.4	13.05 ± 1.1	13.09 ± 0.1	10.4 ± 0.1	25.9 ± 0.3
VP-PS	52.0 ± 0.4	10.6 ± 0.1	5.1 ± 0.1	7.4 ± 0.1	24.8 ± 0.1

The highest glucan was found in the sample from VP-PS, which was expected since Kraft mills carry out pulping via chemicals, which are able to remove most of the contaminants. This leaves a pulp with high amounts of glucan. CR-PS has the highest xylan, lignin and extractive fractions. The high amount of lignin is attributed to the mechanical pulping method used at the corrugated recycle mill, which leaves much of the lignin in the pulp, unlike Kraft pulping where almost all lignin is removed (Bajpai 2015).

The lowest amount of ash was found in the paper sludge sample from the virgin wood pulping mill, which uses only virgin fibre as feedstock. Virgin fibre contains little to no ash, due to the composition of wood. TPR-PS had the highest ash content of the three different paper sludge samples. The tissue printed recycle mill uses recycled fibre to produce various tissue paper products. The high amount of ash, which constitutes mainly calcium carbonate, is due to the presence of ink and fillers in the recycled fibre used to produce the products. Mills that use recycled fibre greatly increases the ash content (Bajpai 2015). The amount of times the fibre has been recycled also increases the ash content, which negatively effects the enzymatic digestibility, since the ash adsorbs irreversibly to cellulase with a stronger affinity than for the cellulosic fibre (Kang et al. 2010).

In a previous study done by Boshoff et al. (2016) various paper sludge samples were collected from pulp and paper mills in South Africa. These samples were characterised and the fermentabilty of each sludge was tested. Among these samples were the tissue printed recycle, corrugated recycle and virgin pulp mills. The study proved the difference in chemical composition within mills at certain interval times, which is expected for this study as well. The chemical composition for these samples is shown in Table 3-5. The largest difference is the glucan content of the virgin pulp, differing from 52% (this study) to 36% (w/w). The CR-PS from this study contained much less ash than the previous study (26% opposed to 40%), while the lignin content is much less (13% compared to the previous value of 20%).

Table 3-5: Chemical composition of paper sludge as determined by Boshoff et al. (2016)

Paper sludge	**Glucan (% w/w)**	**Xylan (% w/w)**	**Lignin (% w/w)**	**Extractives (% w/w)**	**Ash (% w/w)**
TPR-PS	18.5	8.2	9.5	3.8	60.0
CR-PS	23.6	11.0	20.0	5.8	39.6
VP-PS	35.5	17.7	19.3	7.1	20.4

3.3.1.2 Bulk density

The bulk density for the three types of paper sludge is shown in Figure 3-1. The bulk density was tested at five different conditions: 1) dry paper sludge as received from the mill, 2) milled paper sludge, 3) paper sludge pellets, 4) solids residues after fermentation and 5) solid residues after anaerobic digestion. The second and third condition indicates changes in bulk density with various mechanical treatment, while the fourth and last conditions show changes in bulk density after biochemical treatment.

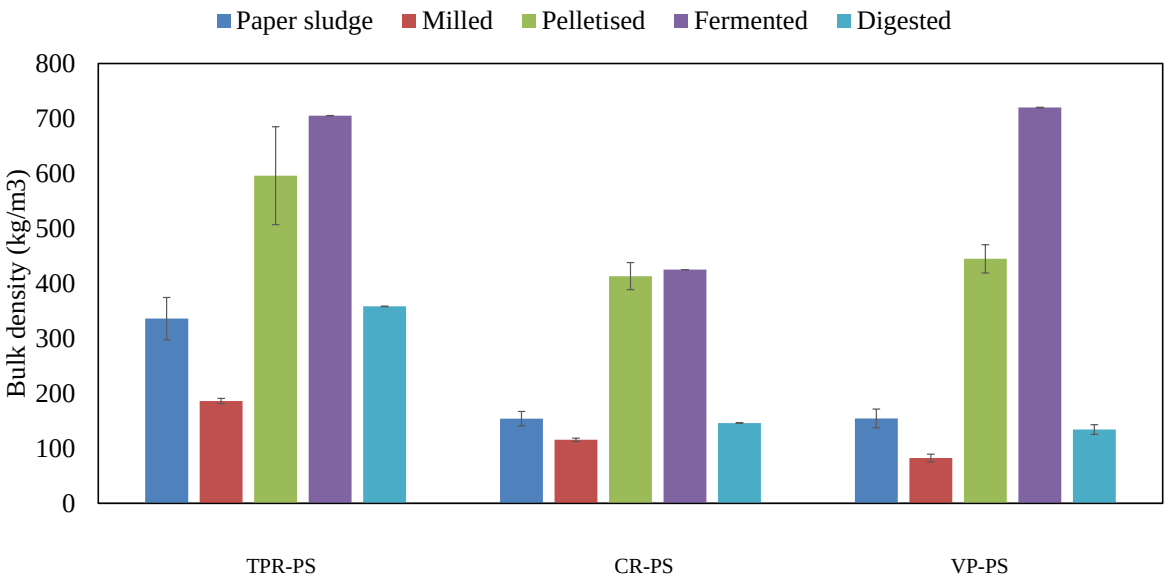

Figure 3-1: Bulk density for paper sludge after mechanical and biochemical treatment

TPR-PS had the highest bulk density (340 kg/m^3), compared to CR-PS and VP-PS (160 kg/m^3 each). This could be because of the higher amount of fillers and ink present in the ash of TPR- PS, resulting in less of the low bulk density fibrous material. Milling paper sludge reduces the bulk density slightly, while pelletising increases the paper sludge density by up to 65% for VP-PS. This high density is ideal for biochemical processing, since reactor space will not be largely occupied with feedstock and will allow for better mixing, as well as providing a more uniform feedstock (Crawford et al. 2015).

Fermented residues show the highest bulk density, since it consists of only lignin and ash, with very little amounts of fibrous material that could lower the bulk density. This is advantageous as a final product, since there are reduced disposal and landfilling costs. Anaerobically digested residues have a similar density to that of untreated paper sludge. This is due to the digested residues still having the fibrous structure, with very little degradation of the fibre component occurring during the digestion process.

3.3.1.3 Water holding capacity

The water holding capacity of paper sludge poses a significant problem with regards to disposal on landfill sites. A high water holding capacity indicates that large volumes of costly water is being sent to landfill, instead of being recycled back to the mill for reuse on site. The mechanical dewatering of paper sludge, through centrifugation or belt and filter pressing, reduces the water content of the paper sludge. However, due to the fibrous structure and the cellulose network there is a natural tendency for paper sludge to retain water. The cellulose fibres in paper sludge are chemically swollen, resulting in a high water holding capacity, which compounds the problem of dewatering and disposal (Lark et al. 1997). The water holding capacity was tested for milled paper sludge, fermented residues and digested residues. The results are shown in Figure 3-2.

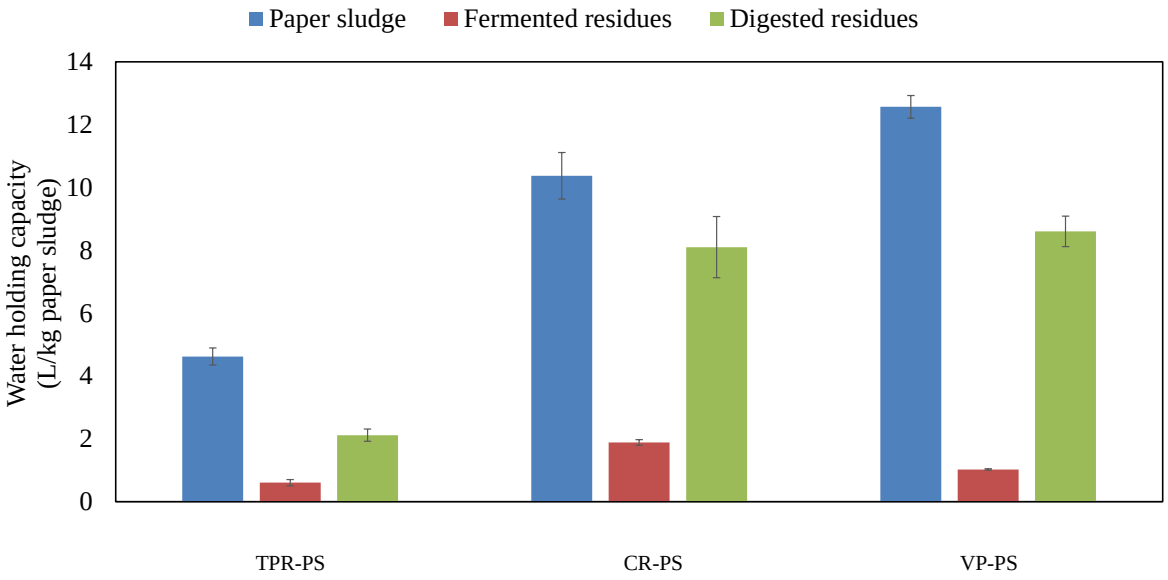

Figure 3-2: Water holding capacity before and after biochemical processing

VP-PS has the highest water holding capacity, possibly due to the longer lengths of the fibre, which are inherent to the chemical pulping process. Mechanical pulping is more intensive, with the grinding and refining stages shortening the fibre lengths, thus reducing the water holding capacity (Boshoff et al. 2016). TPR-PS had the lowest water holding capacity, which could be due to the presence of high amounts of ash and very little fibre, since the fibre component contributes to the water holding capacity of paper sludge (Lark et al. 1997). The

fillers and ink present in the ash are hydrophobic, reducing the water holding capacity of the paper sludge (Kamali & Khodaparast 2015).

The fermentation process decreased the water holding capacity of VP-PS from 12.6 L/kg to 1.0 L/kg for VP-PS. Based on the VP-PS production rate of 35 tonne/day, the water being disposed annually amounts to 164 000 m^3/year. With the water holding capacity being reduced to only 1.0 L/kg due to the fermentation process, theoretically only 14 000 m^3/year of water would be disposed of alongside the paper sludge. This could amount to water savings of 150 000 m^3/year, with the recovered water being sent back to the process after mechanical dewatering of the sludge, such as centrifugation or pressing. Apart from the water savings, there will also be a major reduction in the disposal costs (Bajpai 2015).

The anaerobic digestion process shows a less prominent decrease in water holding capacity, with a reduction from 12.6 L/kg to 8.6 L/kg for VP-PS. This is possibly due to the fact that much of the fibre structure is retained after anaerobic digestion, compared to that of the total loss of fibre structure after fermentation. In comparison with another study on the water holding capacity changes before and after fermentation, CR-PS showed a decrease of 6.6 to 2.6 L/kg, while VP-PS showed a decrease of 8.6 to 4.5 L/kg (Boshoff et al. 2016). Paper sludge tested by Lark et al. (1997) showed a decrease in water holding capacity of up to 60% of the original paper sludge after enzymatic hydrolysis with an enzyme dosage of 5 FPU/g dry substrate and a solid loading of 60 g/L dry substrate. This validates the findings of this study with regards to the decrease in water holding capacity after biochemical processing.

3.3.2 Simultaneous saccharification and fermentation

SSF experiments were conducted in order to determine the extent of conversion of paper sludge to bioethanol, and to use these values in an economic model to determine the profitability and feasibility of the fermentation of paper sludge on an industrial scale. These experiments are scale up experiments, based on the optimal solids loading and enzyme dosage determined by Boshoff et al. (2016) and Robus et al. (2016). Paper sludge from new mills were selected to increase the knowledge base of all the paper and pulp mills in South Africa. The SSF experiments were also used as part of the comparison study between bioethanol or biogas as the most economical feasible product of paper sludge biological conversion.

3.3.2.1 Tissue printed recycle paper sludge ethanol concentration

TPR-PS had the highest ash content (63% w/w), shown previously in Table 3-4. The unproductive and irreversible binding of ash to cellulase requires an additional washing step to reduce the ash content to within reasonable amounts (Chen, Han, et al. 2014). The high ash content also reduces the amount of glucose present, making it nearly impossible to reach the desired minimum ethanol concentration of 40 g/L for downstream processing (Kang et al. 2011).

A proposed labscale washing step (Kang et al. 2010; Kang et al. 2011; Chen, Venditti, et al. 2014) entails washing paper sludge at least five times to reduce the ash content to a desirable content. Some washing steps call for 50 times the amount of water for the mass of paper sludge to be washed, typically in laboratory scale experiments (10g paper sludge to 500 ml water) (Gurram et al. 2015). Using a paper sludge to water mass ratio of 1:4 per wash cycle, amounts to 600 tonne clean water used per day, based on a minimum paper sludge flow rate of 30 dry tonne per day. Not only does it require significantly large amounts of water in a water scarce country, but also creates an additional waste water stream that needs to be treated. Robus et al. (2016) reported a loss of 9% of the cellulose fibres during washing, which relates to a water stream containing almost 10% of the paper sludge that was initially fed. Chen, Venditti, et al. (2014) reported a paper sludge flow rate of 3500 kg/h for a washed paper sludge fermentation plant, producing ethanol at 157 kg/h, but with a waste water stream of 590 kg/h. Another disadvantage of washing as a pre-treatment step is the increase in equipment cost, as well as an increase in energy required (Van Dyk & Pletschke 2012). For these reasons, paper sludge was used as received from the mills, with no washing step.

Another difficulty surrounding the fermentation of high ash paper sludge, is the low glucose percentage in the paper sludge, typically around only 20% (w/w) (Robus et al. 2016), which impacts the ethanol concentrations that can be reached when operating at a low solids loading. In order to overcome this, the proposed solids loading of 210 g/L fed solids as optimised by Robus et al. (2016), can be increased until an acceptable ethanol concentration can be reached. If the solids loading is increased from 210 g/L to 330 g/L, a theoretical ethanol concentration of 35 g/L can be reached, using Equation (2-3. This falls within the current state of technology for paper sludge, since fermentations using VP-PS reached 34 g/L (Boshoff et al. 2016). This solids loading will lead to four extra feedings. The ethanol concentration profile for the fermentation of TPR-PS is shown in Figure 3-3. Each feeding is indicated with an arrow, the last feeding was at 120 hours.

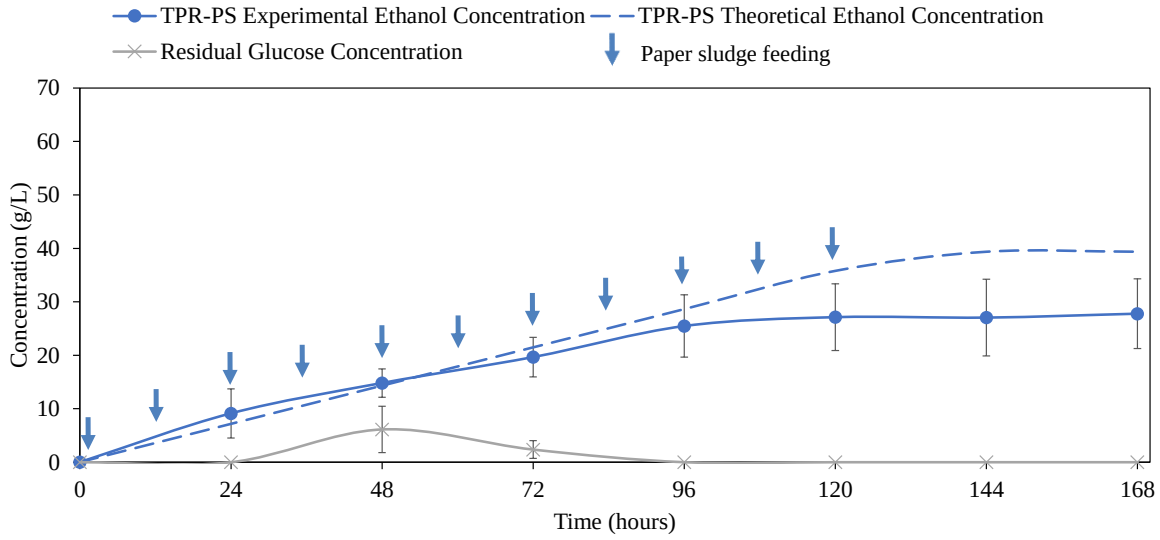

Figure 3-3: TPR-PS ethanol and residual glucose concentration profiles for fed-batch fermentation

The final ethanol concentration was 27.8 ± 6.5 g/L, with an ethanol yield that was 70.6% of the theoretical maximum, and a productivity of 0.165 g/L/h. This ethanol concentration does not reach the minimum required of 40 g/L for cost effective downstream processing. The experimental ethanol concentration is slightly higher than the theoretical ethanol concentration until 48 hours, which could be attributed to the method used to determine the chemical composition (Boshoff et al. 2016). The high amount of ash in TPR-PS buffers the acid used in

the acid hydrolysis step, which could cause the amount of glucose to be underestimated (Sluiter et al. 2008a). The residual glucose concentration peaked at 48 hours, at 6.1 g/L.

The relatively high ethanol yield of 70.6% could be due to the low amount of lignin (6.4% w/w as shown in Table 3-4) present in the paper sludge. The decreased amount of lignin present in the paper sludge will increase the efficiency of the hydrolysis, since there is very little lignin to bind irreversibly to the enzymes (Kadam et al. 2004). TPR-PS has undergone a mechanically and chemically intensive recycling process, shortening the length of the fibres which makes paper sludge less resistant to enzymatic attack. This decrease in resistance increases the amount of monomeric sugars in the broth which can be converted by yeast to ethanol, thus increasing the overall ethanol concentration (Chen, Han, et al. 2014).

The high bulk density of 590 kg/m^3 (Figure 3-1) and the low water holding capacity of only 4.6 L/kg (Figure 3-2) could result in a less viscous broth, and enzymes can come into contact with the paper sludge since there is free water available which allows for adequate mixing (Elliston et al. 2013). This could be the reason why the high solids loading of 330 g/L could be reached, without significantly impacting the agitation within the bioreactor (Geng et al. 2015). It can be seen on Figure 3-3 that there is no discernible increase in ethanol concentration after 96 hours, despite the addition of three more feedings. This could be an indication of irreversible binding of ash to the enzymes, thus halting the release of monomeric sugars and stopping the production of ethanol (Kang et al. 2011). The lack of residual glucose in the reactor after 96 hours indicates that there is possibly very little enzymatic hydrolysis taking place, the plateau in the ethanol concentration corroborates this (Kristensen et al. 2009).

The initial pH dropped from 5.8 to 5.6 during the fermentation. In a study by (Kang et al. 2010), it was found that carbonic and organic acids (lactic acid, acetic acid) were produced during fermentation, and these acids interacted with the ash (present as calcium carbonate) to form calcium acetate and calcium lactate buffers, which lowers the pH.

Lark et al. (1997) conducted batch fermentations using recycled paper sludge at 190 g/L and an enzyme dosage of 8 FPU/g PS, achieving an ethanol yield of 34 g/L and a conversion of 73%. This is both a lower enzyme dosage and lower solids loading, resulting in better ethanol concentrations which are attributed to the higher glucan content of between 56% and 59% in the recycled paper sludge. This study shows that higher ethanol concentrations are achievable from recycled paper sludge, depending on the amount of glucan found in the sample.

3.3.2.2 Corrugated recycle paper sludge ethanol concentration

The following section details the conversion of CR-PS to ethanol. The ethanol concentration profile for CR-PS is shown in Figure 3-4, with each feeding indicated with an arrow.

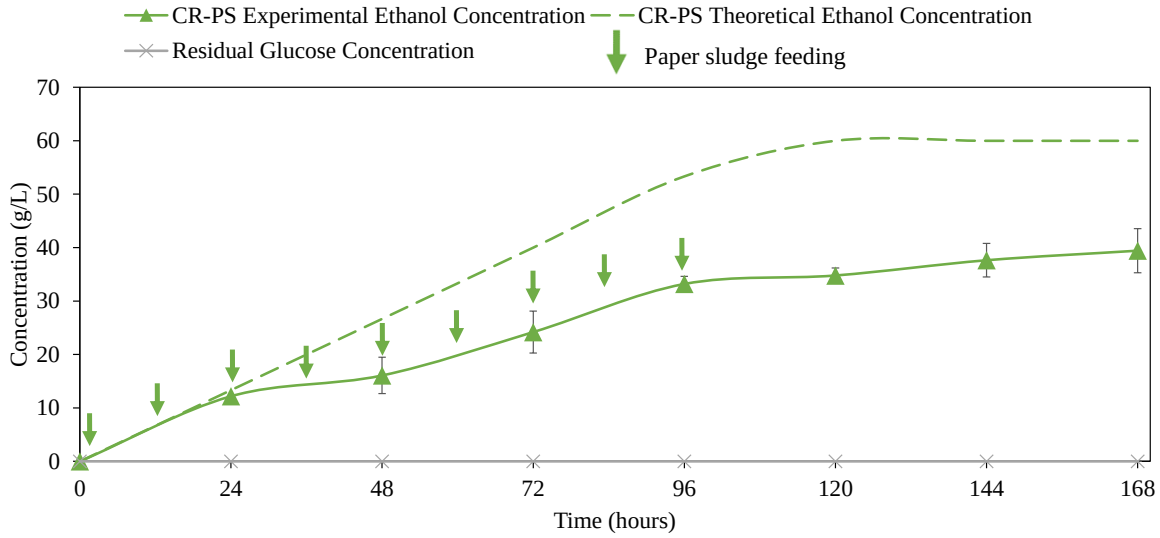

Figure 3-4: CR-PS ethanol and residual glucose concentration profiles for fed-batch fermentation

The last batch of paper sludge was added at 96 hours, where after the ethanol profile can be seen to plateau to a final ethanol concentration of 39.4 ± 4.1 g/L. This ethanol concentration corresponds to a conversion of only 65.7% of the theoretical maximum. A productivity of 0.235 g/L/h was achieved.

The low conversion of only 65.7% can be attributed to several factors. CR-PS has a lignin content of 13.3 % (w/w), as indicated in Table 3-4. The presence of lignin due to the mechanical treatment of CR-PS (Boshoff et al. 2016) adds to the recalcitrant nature of CR-PS, which causes the cell wall structure to remain intact thus preventing the access of enzymes to the cellulose. Higher amounts of enzymes will be needed to obtain efficient enzymatic hydrolysis. The low bulk density of the CR-PS pellets, being the lowest of all the PS pellets at 413 kg/m^3 (Figure 3-1), and the high water holding capacity of 10.4 L/kg PS (Figure 3-2) can cause a thick slurry with insufficient mixing within the reactor, which would cause very little free water being available for proper enzymatic hydrolysis. There was no accumulation of

glucose during the reaction, indicating that enzymatic hydrolysis was the rate limiting step (Kristensen et al. 2009).

The enzyme dosage for CR-PS was 29.3 FPU/g glucan, compared to 72.2 FPU/g glucan for TPR-PS and 38.4 FPU/g glucan for VP-PS, previously shown in Table 3-2, with these values based on an optimisation study completed by Boshoff et al. (2016) and Robus et al. (2016). As previously mentioned in Table 3-5, the CR-PS used by Boshoff et al. (2016) had a much higher ash content (39.6% w/w) as well as a lower glucan content (23.6% w/w) than that of the CR- PS used in this study. Despite using an enzyme dosage of 11 FPU/g PS for both SSF reactions, the enzyme dosage in terms of FPU/g glucan was much higher for the CR-PS from Boshoff et al. (2016) at 46.6 FPU/g glucan.

The enzyme dosage per gram glucan was possibly too low, and a way to solve this problem would be to increase the enzyme dosage to that of 46.6 FPU/g glucan (or 17.5 FPU/g PS), with the higher enzyme dosage being able to overcome the problems with high lignin and high viscosity in the broth. An increase in enzyme dosage will increase the production costs, however it will result in higher ethanol yields which will increase the profit margin (Zhang & Lynd 2010).

3.3.2.3 Virgin pulp paper sludge ethanol concentration

The ethanol concentration profile for VP-PS is shown in Figure 3-5.

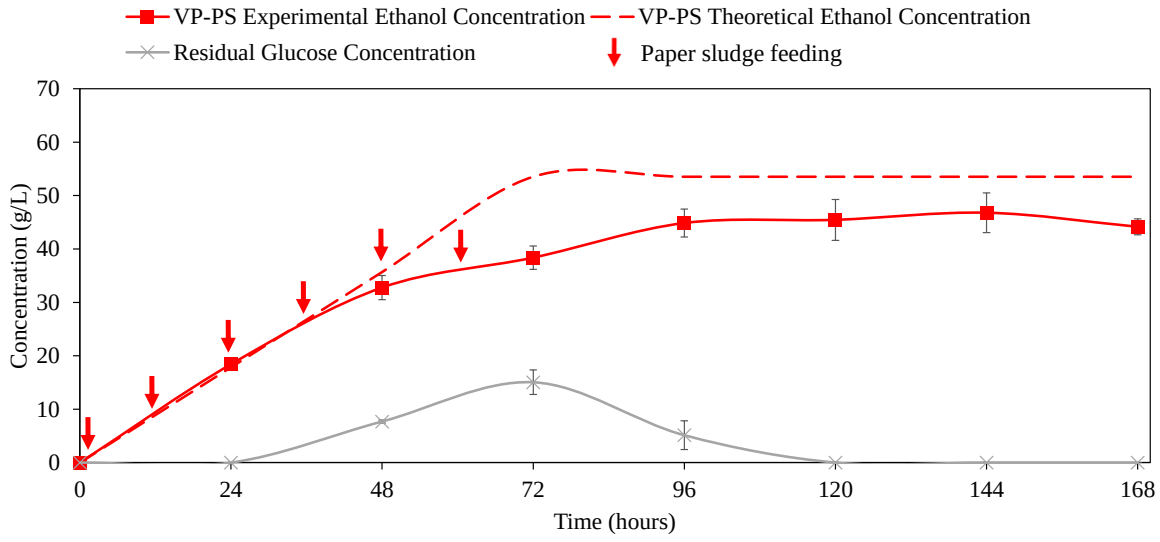

Figure 3-5: VP-PS ethanol and residual glucose concentration profiles for fed-batch fermentation

The highest ethanol concentration is 46.8 ± 3.7 g/L, with a conversion of 87.4% of the maximum theoretical yield, with a corresponding productivity of 0.325 g/L/h. The final feeding was added at 60 hours. It can be seen that the rate of hydrolysis decreased after 48 hours and increased again after 72 hours, likely due to the enzymatic hydrolysis product glucose causing enzyme inhibition (Van Dyk & Pletschke 2012). The fast rate of hydrolysis up until 48 hours can be attributed to the depletion of the cellulose that is easily accessible, resulting in the decreased rate of hydrolysis after 48 hours (Wallace et al. 2016). A slight spike in the pH was observed at 72 hours. The residual glucose concentration increases after 24 hours, reaching a maximum of 15.1 g/L at 72 hours. Yeast inhibition occurs at glucose levels of 15 g/L (Almeida et al. 2007). The accumulation of glucose was possibly due to yeast inhibition, however at 72 hours the productivity of the yeast was 0.533 g/L/h ethanol, indicating that the yeast was probably not affected. The glucose accumulation can possibly be reduced by feeding the paper sludge after longer time intervals, or decreasing the size of the feedings.

The enzyme dosage for VP-PS was the highest (20 FPU/g PS as shown in Table 3-2), compared to all the paper sludge types, which could attribute to the high ethanol concentration and conversion. This enzyme dosage was based on an optimisation study conducted by Boshoff et al. (2016), who found that paper sludge from Kraft mills tended to be highly recalcitrant and required high enzyme dosages and low solids loadings. This ensures enough free water for the enzymes to diffuse through the fermentation medium (Van Dyk & Pletschke 2012). Due to the low solids loading of 180 g/L, the water holding capacity (12.6 L/kg) and bulk density (445 kg/m3) would have had no significant effect on the reaction.

Fan et al. (2003) conducted semi-continuous fermentation on Kraft paper sludge, with a slightly higher solids loading of 195 g/L, achieving ethanol concentrations of 50 g/L at a conversion of 74%. These results are similar to that achieved with fed-batch fermentation in this study except there was a higher conversion in this study, possibly due to the lower solids loading used which increased the enzymatic hydrolysis efficiency. Kraft paper sludge batch fermentations completed by Kang et al. (2010), at only 135 g/L solids loading and 22 FPU/g PS yielded a conversion of only 75% with 26 g/L ethanol in the final broth.

3.3.2.4 Residual sugars in fermentation broth

It is important to consider the sugars in the broth, which will give an indication on how the enzymatic hydrolysis is proceeding. The strain of *S. cerevisiae* used in these experiments is not capable of xylose fermentation, so all xylose produced during hydrolysis is expected to remain as residual sugars. The xylose concentration profile for all three paper sludge types is shown in Figure 3-6.

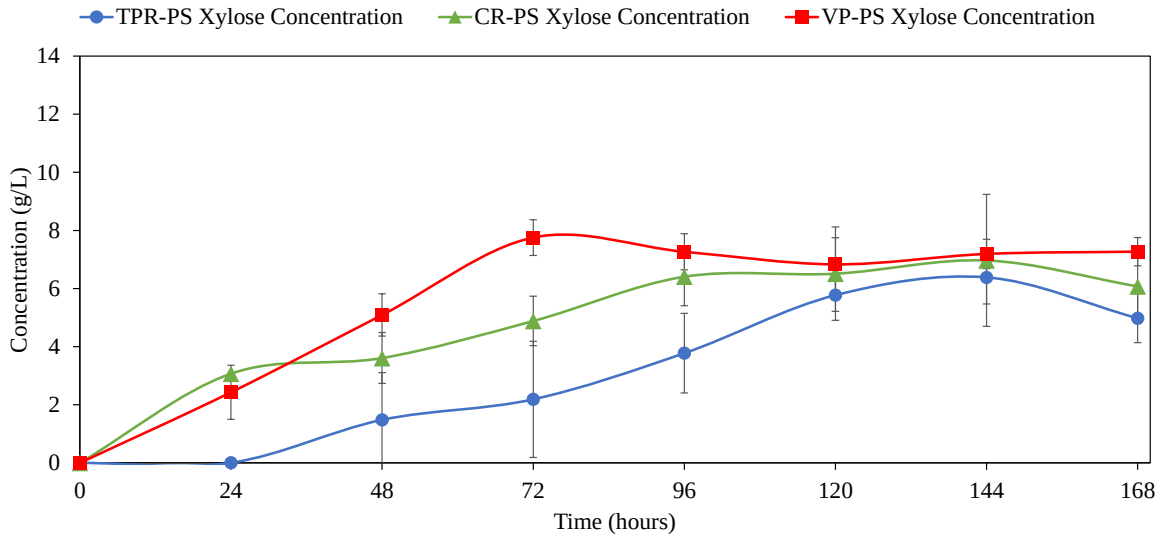

Figure 3-6: Xylose concentration profile

The highest xylose concentrations for TPR-PS, CR-PS and VP-PS were 6.4 ± 0.9, 7.0 ± 2.3 and 7.8 ± 0.6 g/L respectively. The theoretical xylose concentration for TPR-PS was 18.5 g/L, with a conversion yield of 34.2%. In a similar study, using washed TPR-PS, the amount of conversion of xylose ranged from 60.6% to 68.9% during SSF without a xylose utilising yeast (Robus et al. 2016). VP-PS had a similar conversion of 35.5%, with a theoretical xylose concentration of 21.9 g/L. However, in a similar study conducted by Boshoff et al. (2016), a xylose conversion of 50.7% was achieved. CR-PS had a much lower conversion, of only 16.7%, calculated based on a theoretical xylose concentration of 41.8 g/L. Boshoff et al. (2016) obtained a much higher xylose conversion of 60.7% for paper sludge coming from a mill that recycles old corrugated containers. The overall lower conversion indicates a much slower rate of reaction for enzymatic hydrolysis, especially for CR-PS. This correlates to the low ethanol yield of only 65.7%, shown in Figure 3-4, implying an increase in enzyme dosage is needed.

3.3.2.5 Residual sugars in solid residues

The chemical composition of the solid residues after fermentation is given in Table 3-6.

Table 3-6: Chemical composition of solid residues after fermentation

Fermented residues	Glucan (% w/w)	Xylan (% w/w)	Lignin (% w/w)	Extractives (% w/w)	Ash (% w/w)
TPR-PS	2.4 ± 0.1	0.5 ± 0.1	7.0 ± 0.1	20.5 ± 0.1	69.5 ± 0.1
CR-PS	9.3 ± 0.3	2.5 ± 0.1	28.1 ± 0.1	25.0 ± 0.1	35.1 ± 0.2
VP-PS	8.2 ± 0.3	1.8 ± 0.1	25.4 ± 0.1	40.2 ± 0.1	24.4 ± 0.1

The composition of the solid residues after fermentation was compared to the initial composition, indicated in Table 3-4. The initial paper sludge chemical composition was used to calculate the reduction in glucan and xylan after the fermentation process. The reduction in glucan and xylan content is shown in Table 3-7.

Table 3-7: Reduction in glucan and xylan content after fermentation

Paper sludge	Glucan (%)	Xylan (%)
TPR-PS	88.3	90.2
CR-PS	75.2	80.8
VP-PS	84.2	83.2

TPR-PS showed the highest reduction in both the glucan and xylan percentages, possibly due to the low initial sugar content of only 0.21 g glucan/g and 0.05 g xylan/g. Comparing the initial values of TPR-PS to those of VP-PS, which is 0.52 g glucan/g and 0.11 g xylan/g, it can be seen that the presence of sugars in TPR-PS is the limiting factor. The lowest reduction in sugars was for CR-PS, probably caused by the low enzyme dosage rate of only 11 FPU/g paper sludge. In a study by Fan & Lynd (2007b), glucan and xylan conversions of 96.8% and 90.4% were reported for semi-continuous SSF experiments.

3.3.3 Anaerobic digestion

3.3.3.1 Biogas composition

The methane content of biogas produced during anaerobic digestion is given in Table 3-8. The values are based on samples taken every seven days and measured using gas chromatography. The average methane content was calculated as described below, and used to determine the methane produced during anaerobic digestion, described in the section that follows.

Table 3-8: Methane content of biogas

	Methane content (% v/v)		
Time (days)	**TPR-PS**	**CR-PS**	**VP-PS**
7	49.4 ± 4.2	37.4 ± 0.3	46.1 ± 0.2
14	50.4 ± 4.1	61.3 ± 3.9	45.7 ± 4.3
21	50.8 ± 1.2	53.7 ± 1.7	38.5 ± 3.0
28	41.8 ± 5.0	58.0 ± 1.4	42.1 ± 11.9
Average	**48.1 ± 4.3**	**52.6 ± 10.6**	**43.1 ± 3.6**

The TPR-PS gave the lowest methane concentration after 28 days, almost 10% (v/v) lower than the first three weeks (Table 3-8). It can be assumed that after 21 days the digestion was near completion, and the last value was not taken into consideration for calculations on total methane production. The average methane concentration was recalculated to be 50.2 ± 0.4% (v/v).

The average methane concentration for CR-PS has a very high standard deviation, due to the initial low methane value of 37% (v/v). During the first week, there was a relatively large lag phase where the inoculum could have been adjusting to the new feedstock, therefore the final CR-PS methane value was based on the second week onwards, which resulted in an average methane content of 57.7 ± 0.3% (v/v).

The final methane content analysis for VP-PS shows a very high standard deviation of ±11.9% (v/v). The methane content between the two duplicate experiments varied from 33.6% (v/v) and 50.5% (v/v). The first value negatively skewed the methane content, and was disregarded in the calculation of the final methane concentration, which is 44.3 ± 1.7% (v/v).

3.3.3.2 Biogas cumulative volumetric production

This section details the volumetric biogas production during anaerobic digestion. The section is divided in to two parts, with the first relating the biogas produced to the amount of total solids (TS) fed, while in the second section biogas production is related to the volatile solids (VS) fed. The online gas measurement system involved taking a volumetric reading every minute for the entire duration of the run. The results shown are for the average of duplicate runs.

The biogas production relative to the total amount of solids added is shown in Figure 3-7.

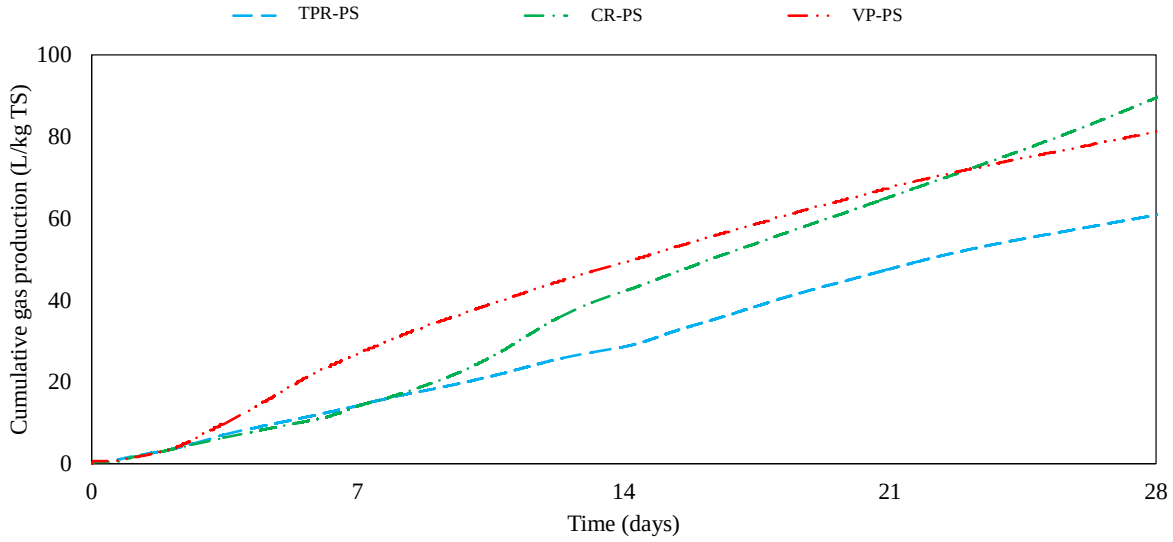

Figure 3-7: Cumulative biogas production per total solids added

The biogas production rate for VP-PS had the smallest lag phase, of only 3 days. This could be due to the reduction in initial solids loading of 6% w/v, opposed to the 10% w/v for TPR- PS and CR-PS as shown in Table 3-3. The lower solids loading resulted in an increased amount of free water for mixing, which would aid in the growth and adjustment of the bacteria in the digester, since water is crucial for adequate cell growth (Serrano 2011). The lower solids loading also allowed for proper mass and heat transfer in the digester, due to much lower viscosity in the digester (Karlsson et al. 2011).

CR-PS had a distinctively longer lag phase, after which there was a rapid increase in biogas production outperforming VP-PS after the third week. The longer lag phase could be due to the low bulk density of milled CR-PS of only 115 kg/m^3 as seen in Figure 3-1, as well as the high water holding capacity of 12.6 L/kg from Figure 3-2, which could cause agitation problems and inadequate mixing (Budzianowski 2016). The initial dry milled paper sludge volume for corrugated recycle was 16.4 L, which is about half of the total digester volume (31 L). This corresponds to the longer lag phase seen, since proper material transfer would be difficult to achieve with the little free water available for mixing (Liao & Li 2015). Liao & Li (2015) describe high solids loading anaerobic digestion (solids loading above 8%) as a pseudo-plastic fluid or sticky semisolid mixture with poor mass transfer efficiency.

TPR-PS showed a steady production of biogas, with a slight increase in the cumulative production after two weeks. The high bulk density of milled TPR-PS of 190 kg/m^3 (shown in Figure 3-1) and low water holding capacity of only 4.6 L/kg, depicted in Figure 3-2, allowed for enough free water to enable sufficient mixing and proper mass transfer within the digester (Mao et al. 2015).

The final gas produced was 62.9 ± 10.8, 94.4 ± 8.3 and 83.9 ± 2.9 L/kg paper sludge for TPR- PS, CR-PS and VP-PS, respectively. These values are however statistically insignificant since an analysis of variance resulted in a *p* value of 0.063 which is greater than 0.05.

VP-PS had the lowest pH of 6.3 ± 0.1, while TPR-PS had a pH of 6.8 ± 0.2. CR-PS had the highest pH of 7.1 ± 0.1. Bacteria are sensitive to pH changes, with an optimum pH ranging between 6.7 and 7.5 for methanogenic bacteria. At a pH lower than 6, methane production might decrease and hydrogen production increase. A decrease in pH might be caused by high amounts of carbon dioxide, in the liquid phase as carbonic acid, as well as the production of acids (Serrano 2011). Low pH can be an indication that the process is still in the hydrolysis and acidogenesis stages, resulting in lower methane concentrations, as seen in VP-PS (Serrano 2011).

Intermittent liquid sampling would have been better to track the pH, however the nature of paper sludge caused the liquid sampling ports to clog, with no flow when the valves were opened. Unclogging the ports would have disrupted the stability of the process and therefore only the final liquid digestate pH was measured.

The cumulative methane production is shown in Figure 3-8. The methane production was obtained from the cumulative biogas production (Figure 3-7) and the average methane content for the 4 weeks, as presented in Table 3-8 and discussed in Section 3.3.3.1.

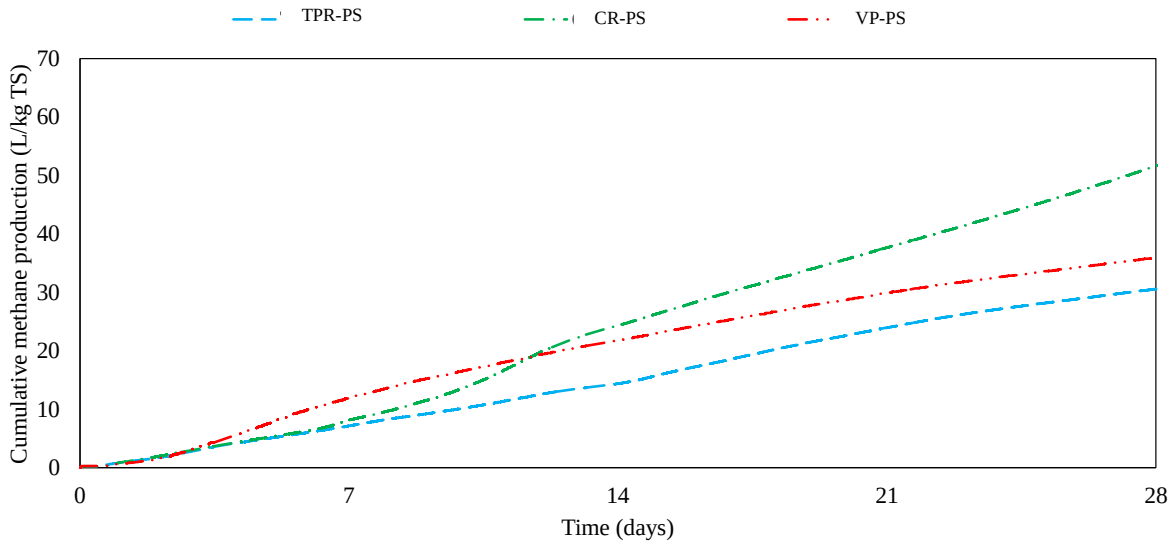

Figure 3-8: Cumulative methane production per total solids added

The final methane production was 31.6 ± 5.7, 54.4 ± 5.1 and 37.2 ± 2.7 L CH_4/kg TS for TPR-PS, CR-PS and VP-PS, respectively. ANOVA results indicate that these values are statistically significant, with a p value of 0.026 ($p < 0.05$). CR-PS is the best producer in terms of both cumulative biogas production and methane gas production, due to the high methane content of the biogas produced (58% v/v). The interesting observation was the close performance of TPR-PS and VP-PS, with the expectation that VP-PS would outperform TPR-PS, considering that TPR-PS consists of predominantly ash (63% w/w). However, as discussed in Section 3.3.2.1, the high bulk density and low water holding capacity of TPR-PS could aid in the material transfer, which would cause an improvement in the hydrolysis and subsequent methane production (Bensmann et al. 2016).

The methane production relative to the amount of volatile solids added is shown in Figure 3-9, based on the cumulative biogas production (Figure 3-7) as well as methane content, shown in Table 3-8 and the volatile solids content calculated from the ash content shown in Table 3-4.

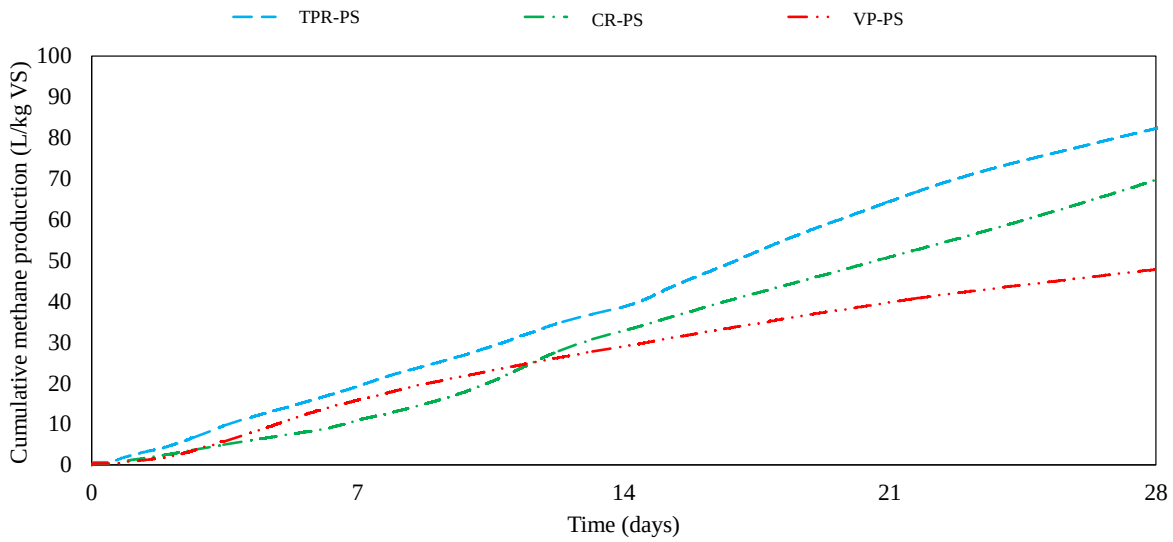

Figure 3-9: Cumulative methane production per volatile solids added

TPR-PS produced 85.0 L CH_4/kg VS added, while CR-PS produced 73.5 L CH_4/kg VS. VP- PS produced only 49.4 L CH_4/kg VS. The *p* value (0.068) from an ANOVA suggests that these values are statistically insignificant. TPR-PS outperformed both VP-PS and CR-PS, based on the amount of volatile solids added. This is due to the fact that TPR-PS had only 37% volatile solids per total solids, while CR-PS and VP-PS both consists of 75% volatile solids (shown in Table 3-4). This makes anaerobic digestion an attractive biochemical processing route for substrates with high ash contents.

Similar methane productions were observed by Jokela et al. (1997), with primary paper sludge producing 45 L CH_4/kg VS added. Slightly higher methane productions were observed by Hagelqvist (2013) and Huiliñir et al. (2014) of 53 and 83 L CH_4/kg VS respectively. In a study by Bayr & Rintala (2012), Kraft paper sludge yielded a methane production of 210 L CH_4/kg VS, these were however conducted in 1 L static digesters and for a longer retention time of 42 days.

3.3.3.3 Residual sugars after digestion

There were no free sugars detected in the final liquid digestate. This can be an indication of the "convert & utilise" nature of the bacteria. There should be no build-up of sugars, rather sugars are immediately converted from the hydrolysis stage to the acidogenesis stage (Labatut 2012).

3.3.3.4 Agitation

Viscosity problems occurred due to incomplete mixing, with only the material at the bottom of the reactor close to the single impeller being completely homogenised (data not shown). This is a common problem and was also reported by Karlsson et al. (2011). Hydrolysis is usually the rate limiting step in the production of methane, especially in solid digestion. The hydrolytic enzymes produced by the bacteria need to be produced in large amounts and need to make contact with the substrate, with incomplete mixing lead to poor hydrolysis (Qi 2001).

The solids loading for anaerobic digestion is usually less than 15%, since adequate bacteria cell growth requires large amounts of water. Material transfer also becomes limited when there is inadequate free water for proper mixing (Serrano 2011).

3.4 Variance analysis for biochemical processes

After the completion of both fermentation and anaerobic digestion, an analysis of variance (ANOVA) was completed. The results are shown in Table 3-9. The ANOVA was completed on the experimental ethanol concentration results (g/L) for the triplicate fermentation runs as well as the methane yield (L CH_4/kg PS) for the duplicate anaerobic digestion experiments.

Table 3-9: Variance of paper sludge for biochemical processing

	Fermentation	**Anaerobic digestion**
TPR-PS	42.7	29.6
CR-PS	17.0	23.1
VP-PS	2.2	1.6

Throughout both fermentation and anaerobic digestion, TPR-PS showed an increased amount of variance, while VP-PS had comparatively low variance. This can be attributed to the feedstock used in mills using recycled fibre from different sources and different grades (Bajpai 2015). VP-PS had relatively small standard deviations in both fermentation and digestion experiments, discussed in Section 3.3.2 and Section 3.3.3, which can be attributed to the steady supply of virgin feedstock used at Kraft mills (Boshoff et al. 2016), and is seen in Table 3-9 with a variance of only 2.2 for fermentation, and 1.6 for anaerobic digestion.

3.5 Energy conversions for fermentation & anaerobic digestion

The gross energy conversion was calculated for the bioethanol and biogas yields. The higher heating values (HHV) for ethanol and methane are 29.85 and 55.53 MJ/kg, respectively. The energy yields are shown in Table 3-10.

Table 3-10: Energy balance for fermentation and anaerobic digestion

	Fermentation - bioethanol			**Anaerobic digestion - methane**		
	TPR-PS	**CR-PS**	**VP-PS**	**TPR-PS**	**CR-PS**	**VP-PS**
Product yield (kg/tonne PS)	98.20	146.03	259.87	20.7	35.7	24.4
Product energy yield (MJ/tonne PS)	2930	4360	7760	1150	1980	1350

Based on the energy yields, the fermentation process seems to be the more attractive biochemical processing route. While ethanol provides less energy per mass unit (29.85 MJ/kg ethanol vs. 55.53 MJ/kg methane), the production rate for ethanol is much higher, resulting in a larger energy return. However, additional economic factors also play a role in determining the most feasible biochemical processing route. This will be explored further in Chapter 4.

3.6 Summary and conclusion

The results for the fermentation experiments are summarised in Table 3-11. The SSF conditions for solids loading and enzyme dosage is listed, as well as the final ethanol concentration achieved and the conversion calculated based on Equation (3-10) and (3-11).

Table 3-11: Summary of fermentation results

	TPR-PS	**CR-PS**	**VP-PS**
Enzyme dosage (FPU/g PS)	15	11	20
Solids loading (g/L)	330	270	180
Ethanol concentration (g/L)	27.8	39.4	46.8
Conversion (%)	70.6	65.7	87.4
Productivity (g/L/h)	0.165	0.235	0.325

The fermentability and digestibility of three types of paper sludge was studied, focussing on scale up experiments as opposed to lab scale experiments. Fermentations were completed in 20 L bioreactors, with VP-PS obtaining the highest ethanol concentration of 46.8 g/L, while CR-PS only yielded 39.4 g/L and TPR-PS the lowest concentration of 27.8 g/L. It was observed that high bulk density as well as low water holding capacity improved the fermentation performance. Enzyme dosages below 35 FPU/g glucan resulted in poor enzymatic hydrolysis efficiencies.

Anaerobic digestion experiments were conducted in 30 L digesters, without nitrogen sparging in order to simulate industrial conditions. The highest methane content in the produced biogas, was 58% (v/v) and was produced during the digestion of CR-PS. The highest volumetric methane production was also for CR-PS, producing 54 L of methane per kg paper sludge added. VP-PS produced 37 L/kg while TPR-PS produced only 32 L/kg.

The methane yields from paper sludge is summarised in Table 3-12. The highest methane yield was obtained from CR-PS, at 36 kg methane/tonne paper sludge.

Table 3-12: Yields from anaerobic digestion of paper sludge

	TPR-PS	**CR-PS**	**VP-PS**
Total gas production (L/kg PS)	62.9 ± 10.8	94.4 ± 8.3	83.9 ± 2.9
Methane content (% v/v)	50.2 ± 0.4	57.7 ± 0.3	44.3 ± 1.7
Methane yield (m^3/tonne PS)	31.6 ± 5.7	54.4 ± 5.1	37.2 ± 2.7
Overall methane yield (kg/tonne PS)	20.7 ± 3.7	35.7 ± 3.3	24.4 ± 1.8

Throughout both fermentation and anaerobic digestion experiments, VP-PS showed the lowest amount of variance between runs, while TPR-PS showed the highest variance. This is attributed to the feedstock used at the various mills, differing from virgin fibre for virgin pulp mills, and recovered fibre used at tissue printed recycle mills.

Based on the experimental results and the energy comparison of the proposed biochemical processes (Section 3.5), a full techno-economic evaluation will be done in Chapter 4, highlighting the economic differences between the two proposed scenarios, for the three types of paper sludge. This is the first step towards developing an implementation strategy at pulp and paper mills in South Africa for bioprocessing of the paper sludge waste stream. The three experimental indicators (yield from feedstock, final concentration and rate of production) from the experimental section will be used in Chapter 4 to develop the techno-economic models.

Chapter 4: Techno-economic evaluation of the production of bioethanol and biogas from paper sludge

4.1 Introduction

The production of biofuels from paper sludge has been proven to be technically achievable from experiments, however the economic feasibility still needs to be established. Some economics studies have been conducted on the economic feasibility of the fermentation process (Chen, Venditti, et al. 2014; Robus et al. 2016), however there is very little available on the economic feasibility of the production of biogas from paper sludge alone. Key economic indicators as well as sensitivities to process changes need to be determined. The objective of this chapter is to investigate and discern between the two biochemical processing routes in terms of process energy efficiency as well as deliverable yields. To the best of the author's knowledge, this is the only experimental and economic comparison study of both biogas and ethanol production from paper sludge, while others have only looked at the experimental part (Kemppainen et al. 2012).

The evaluation process is shown in Figure 4-1. In order to start the economic evaluation, process flow diagrams need to be developed from experimental work to a process that can be applied on an industrial scale. These process diagrams can then be used as input to develop Aspen Plus models, in order to complete the mass and energy balances, determine the required utilities requirement as well as sizing of equipment. Once the costing has been done, the values obtained for capital and operating expenditure are used in the cash flow analysis to determine the key economic indicators, specifically the minimum fuel selling price. Changing some of the process parameters can have an effect on the indicators, which can be observed in a sensitivity analysis.

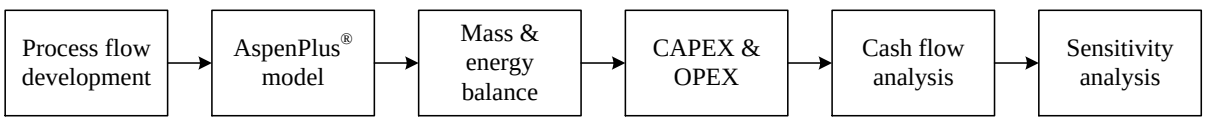

Figure 4-1: Techno-economic evaluation process

4.2 Methods

4.2.1 Process development

4.2.1.1 Fermentation process

The process flow diagram (PFD) for fermentation was developed by modifying process simulations from Robus et al. (2016), Petersen (2015), Gurram et al. (2015) and Fan & Lynd (2007a). These models were updated with experimental results obtained for a larger range of paper sludge types: results from three mills as opposed to only one type of feedstock. These models also include experimental results from larger scale experiments: 20 L as opposed to 200 ml, giving more reliable model predictions. The PFD can be seen in Figure 4-2. There are four main areas: 1.) Feedstock handling, 2.) Fermentation, 3.) Product recovery and 4.) Storage.

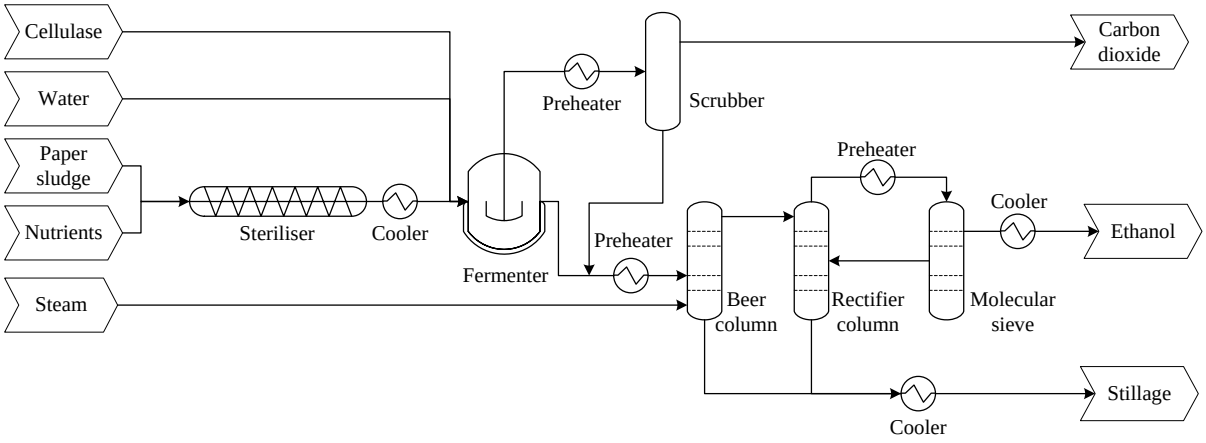

Figure 4-2: Process flow diagram for fermentation of paper sludge to produce ethanol

Feedstock handling

Paper sludge and nutrients (corn steep liquor and magnesium sulphate) are mixed and sent to a screw steriliser with direct steam injection, for 30 minutes at 121°C. This is to ensure thorough sterilisation without any cold spots, in order to prevent possible contamination of the feedstock by *Lactobacillus fermentum*, *L. salivariu* and *L. casei* (Robus et al. 2016). The sterilised material is then cooled down to 37°C, prior to entering the fermenters (Tao et al. 2014).

Fermentation

The proposed fermentation setup is a train consisting of two fermenters in series, which allows for better conversion of paper sludge, since the first reactor is operated at high viscosity but the second fermenter requires drastically less mixing energy, since some of the solids have already been hydrolysed (Shao et al. 2009). The number of trains can be varied to reduce the size of the reactors, to within practical building boundaries (Fan & Lynd 2007a). The total residence time is six days to ensure complete conversion of all the paper sludge, as discussed in Section 3.3.2.

Product recovery

The vent from the fermenter is sent to a scrubber for carbon dioxide removal, with residual amounts of ethanol being recycled back to the beer column (Petersen 2015). The beer from the fermenter is preheated prior to entering the beer column, with 99.9% (w/w) of the ethanol being recovered and sent to the rectifier column. The beer column is steam injected due to the high ash content of the entering beer which will cause fouling (Petersen 2015). The rectifier column purifies the ethanol to 92.5% (w/w). The molecular sieve further purifies the ethanol to 99.5% (w/w), with a recycle stream back to the rectifier column (Fan & Lynd 2007a).

Storage

The final ethanol product is cooled and sent to storage. The stillage from the beer and rectifier column are cooled and sent to the waste water treatment section of the mill. Tanks for enzymes and nutrients, for seven days of operation, are also kept in the storage area (Chen & Fu 2016).

4.2.1.2 Anaerobic digestion process

The process flow diagram (PFD) for anaerobic digestion was developed by modifying the waste water treatment section of the process from Humbird et al. (2011), as well as design philosophies from Shao et al. (2012), Park et al. (2012) and Dalwai (2012). Experimental data from 30 L biodigesters, as discussed in Chapter 3, was used in the models. The PFD can be seen in Figure 4-3.

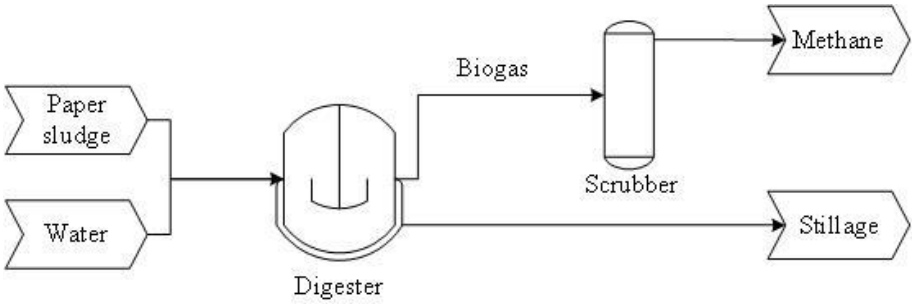

Figure 4-3: Process flow diagram for anaerobic digestion of paper sludge to produce methane

The anaerobic digestion process is much less intricate compared to that required for fermentation, and consists of a steel digester with a cover that is fed with paper sludge and water (Humbird et al. 2011), and an initial amount of bacteria. The stillage is routed to the waste water treatment area of the mill (Aguilera & Ortiz 2016).

4.2.1.3 Feed input for biochemical processing

The flow rate for dry paper sludge is given in Table 4-1. The current paper sludge production rates for the various mills are used (personal communication, 2016), intending that all the paper sludge produced is used in the biochemical conversion plant. Chen, Venditti, et al. (2014) suggest sourcing additional paper sludge from other mills to improve the feasibility of the plant, however this scenario will not be included in the study. The flow rates were calculated based on an uptime of 96% (Humbird et al. 2016). Make up water is added to achieve the desired solids loading for fermentation and anaerobic digestion, as determined in Chapter 3. The nutrients required for fermentation processing were calculated based on experimental values determined by Kadam et al. (1997). It was found that an inexpensive growth medium consisted of 3 g/L corn steep liquor and 0.62 g/L magnesium sulphate. The required amount of enzyme is based on an industrially available cellulase with an activity of 140 FPU/ml, and the dosages for each paper sludge as discussed in Section 3.2.2.

Table 4-1: Feed input for the simulation of the fermentation and anaerobic digestion biochemical processes

Paper sludge	**Production rate (dry tonne/day)**	**Moisture content (% w/w)**	**Fermentation**				**Anaerobic digestion**
			Make up water (tonne/day)	**Corn steep liquor (tonne/day)**	**Magnesium sulphate (tonne/day)**	**Enzyme (tonne/day)**	**Make up water (tonne/day)**
TPR-PS	65.97	48	65.96	0.62	0.13	7.07	681.29
CR-PS	9.64	75	0.01	0.12	0.03	0.76	79.49
VP-PS	35.67	72	64.90	0.61	0.12	5.10	606.02

4.2.2 Aspen Plus® model development

4.2.2.1 Fermentation

The reactor conversions are shown in Table 4-2. It is assumed that all of the solid carbohydrates are converted to glucose and xylose, and that the extractives, lignin and ash are inert (Humbird et al. 2011). It is assumed that xylose is also converted to ethanol, however this has not been proven in the experimental work since *S. cerevisiae* was used, but is anticipated to be true in the near future, with several research going into the development of pentose utilising yeast strains (Smith et al. 2014; Klinke et al. 2004). The conversion values were discussed in Section 3.3.2.

Due to the low conversion of CR-PS of 66%, a theoretical conversion assumption for corrugated recycle, where the theoretical ethanol conversion obtained for corrugated recycle is 75% instead of the experimentally determined 66%, by increasing in enzyme dosage from 11 FPU/g dry substrate to 20 FPU/g dry substrate and assuming a conservative 75% conversion. This will increase the enzyme dosage from 0.76 tonne/day to 1.38 tonne/day.

Table 4-2: Conversion reactions for fermentation

Reaction	Conversion			
	TPR-PS	**CR-PS**	**CR-PS 75% conversion**	**VP-PS**
Glucan + water → glucose	1	1	1	1
Xylan + water → xylose	1	1	1	1
Glucose → 2 ethanol + 2 carbon dioxide	0.7060	0.6572	0.7500	0.8740
3 Xylose → 5 ethanol + 5 carbon dioxide	0.7060	0.6572	0.7500	0.8740

To accommodate for the differences in the paper sludge flow rates between the three mills, the design specification boundaries were changed for the scrubber and distillation columns so that the models will converge.

4.2.2.2 Anaerobic digestion

The conversion reactions for the digester is shown in Table 4-3, which is based on the reactions used by Humbird et al. (2011) in their anaerobic digestion wastewater treatment area. However, it is assumed that only the solid carbohydrates are converted to methane and carbon dioxide, while the extractives, lignin and ash remain inert. The extractives and lignin are not digested in the relatively short retention time of four weeks considered in this anaerobic digestion model (Serrano 2011). The conversion factor was calculated based on stoichiometric calculations to achieve the methane yields determined in Section 3.3.3.2.

Table 4-3: Conversion reactions for anaerobic digestion

Reactions	**Conversion**		
	TPR-PS	**CR-PS**	**VP-PS**
Glucan + water → 3 methane + 3 carbon dioxide	0.2716	0.2364	0.1308
2 Xylan + 2 water → 5 methane + 5 carbon dioxide	0.2716	0.2364	0.1308
Glucose + water → 3 methane + 3 carbon dioxide	0	0	0
2 Xylose + 2 water → 5 methane + 5 carbon dioxide	0	0	0
Extractives + water → 3 methane + carbon dioxide	0	0	0
Lignin + 4.5 water →4.25 methane + 3.75 carbon dioxide	0	0	0

4.2.3 Capital and operating expenditure

The economic models were based on the complete mass and energy balances from the process simulation. The cost analysis was performed for brown field plants, using the existing infrastructure available at the paper and pulp mills (Humbird et al. 2011). The October 2016 exchange rate of R13.87/$ was used.

4.2.3.1 Equipment cost

The equipment costs for common equipment such as pumps, compressors and flash drums were estimated based on values from Aspen Plus, while specialised equipment costs were estimated based on a previous technical report (Robus et al. 2016), with the baseline equipment size rescaled using an exponential scaling equation, given in Equation (4-1) by Humbird et al. (2011). The scaling exponent depends on the characteristic of the equipment. The scaling exponents used were based on values given by Humbird et al. (2011).

$$Purchased\ cost = base\ cost \times \left(\frac{size}{base\ size}\right)^{scaling\ exponent} \quad (4\text{-}1)$$

Purchased equipment costs were adjusted using the plant cost index to a basis year of 2016. The cost index for 2016 was based on the available index for January 2016 (Jenkins 2016). The formula used to calculate the 2016 cost is given in Equation (4-2) as described by Humbird et al. (2011).

$$2016\ cost = base\ cost \times \frac{2016\ cost\ index}{base\ year\ index} \quad (4\text{-}2)$$

Installed equipment costs were calculated using an installation factor multiplied by the purchased cost. The installation factors were based on values from Humbird et al. (2011).

4.2.3.2 Capital expenditure

The capital expenditure (CAPEX) was determined using equipment costing, explained in detail by Humbird et al. (2011). The total direct cost (TDC) includes the sum of all the installed equipment costs, as well 4% of the installed cost for warehousing, 9% of the installed cost for site development and 4.5% of the installed cost for additional piping. The total indirect cost (TIC) is 60% of the TDC, with 10% for prorateable expenses, 10% for field expenses, 20% for home office and construction fees, 10% for project contingency and 10% for other costs (permits, start-up). The fixed capital investment (FCI) is the sum of direct and indirect costs. The working capital (WC) is determined as 5% of the FCI, while the total capital investment (TCI) is the sum of the FCI and the WC.

4.2.3.3 Operating expenditure

The operating expenditure (OPEX) is divided into variable operating costs (feed material) and fixed operating costs (labour and maintenance). Variable operating costs are made up of the material and utility costs, which are calculated from the Aspen Plus mass and energy balance and the costs which are shown in Table 4-4.

Table 4-4: Material and utility costs

Chemical	Cost	Reference
Corn steep liquor/tonne	R2 050	Robus et al. (2016)
Magnesium sulphate/tonne	R4 990	Robus et al. (2016)
Enzyme/tonne	R2 140	Robus et al. (2016)
Electricity/kWh	R0.84	Personal communication mill personnel (2016)
Steam/tonne	R140	Personal communication mill personnel (2016)
Fresh water/tonne	R16.96	Personal communication mill personnel (2016)
Residue transport/tonne	R77.46	Personal communication mill personnel (2016)

Fixed operating costs include the labour and maintenance part of the mill. Two operators are needed per eight hour shift, at a competitive salary of R450/shift (Personal communication with mill personnel, 2016). The labour burden is calculated as 90% of the total salaries per year, and includes costs incurred by staff such as safety, security and janitorial services. Overhead costs include maintenance, which is calculated at 3% of the purchased equipment cost, as well as property insurance, which is calculated as 0.7% of the fixed capital investment. The total operating cost is the sum of the variable and fixed operating costs (Humbird et al. 2011).

4.2.4 Cash flow analysis

Once the CAPEX and OPEX have been determined, the cash flow rate analysis can be done. This involves finding the internal rate of return (IRR) that yields a net present value (NPV) of zero, at a fixed fuel selling price. Another approach is fixing the discount rate at 12%, and calculating the minimum fuel selling price (MSP) that will yield a NPV equal to zero (Robus et al. 2016).

A real term approach was taken, to eliminate the uncertainty of having to predict future prices as is the case for the nominal term approach (Petersen 2015). The income tax rate is fixed at 28%, and is only taken into account if the net revenue in that year is positive. The annual sales is calculated based on the sale of fuel and the avoided disposal cost (Robus et al. 2016). The production costs include the cost of feedstock (which in the case of paper sludge is zero) and the total operating costs. The depreciation charge is calculated as the write off each year due to depreciation on the fixed capital investment, with straight line depreciation (Petersen 2015).

The plant has an expected life time of 30 years (Petersen 2015). The net revenue is calculated as the annual sales minus the cost of production and the depreciation charge. The income tax is calculated on the net revenue, but is only charged if the net revenue is positive. The annual cash income is calculated as the annual sales minus the production costs and income tax (Humbird et al. 2011). The discount factor is calculated using Equation (4-3).

$$Discount\ factor = \frac{1}{(1 + discount\ rate)^{year}} \tag{4-3}$$

The annual present value is equal to the product of the annual cash income and the discount factor. The net present value is equal to the sum of the annual present values minus the total capital investment (Gutierrez et al. 2016), and is shown in Equation (4-4). The NPV is then solved to yield a value of zero by changing either the IRR or the MSP (Humbird et al. 2011).

$$NPV = -TCI + \sum_{t=0}^{N} \frac{positive\ cash\ income}{(1 + discount\ rate)^{t}} \tag{4-4}$$

4.2.5 Energy comparison

The higher heating values (HHV) for the feedstock and products are shown in Table 4-5. These values are used in the calculation for the energy input and output.

Table 4-5: HHV values for feedstock and products

Substrate	HHV (MJ/kg)	Reference
TPR-PS	12.10	Ridout et al. (2016)
CR-PS	16.04	Boshoff et al. (2016)
VP-PS	17.29	Louw et al. (2016)
Ethanol	29.85	
Methane	55.53	
LPG	46.10	

The energy ratio is calculated according to Equation (4-5). The energy ratio is used to quantify the energy efficiency of the biochemical conversion of the feedstock. A value less than 1 indicates that energy is being gained.

$$Energy\ ratio = \frac{\sum energy\ inputs}{\sum energy\ outputs} \quad (4\text{-}5)$$

4.3 Results and discussion

4.3.1 Fermentation techno-economic analysis

4.3.1.1 Energy balance and utility requirements

The energy balance comparing the required input energy and output energy is shown in Figure 4-4. The process energy is made of the heat duties required for chilled water, the cooling tower water, electricity and steam. The highest energy demand during fermentation is for steam in the steam-injected screw steriliser, and for the cooling water required to cool the paper sludge after sterilisation, down to the required fermentation temperature of 37°C.

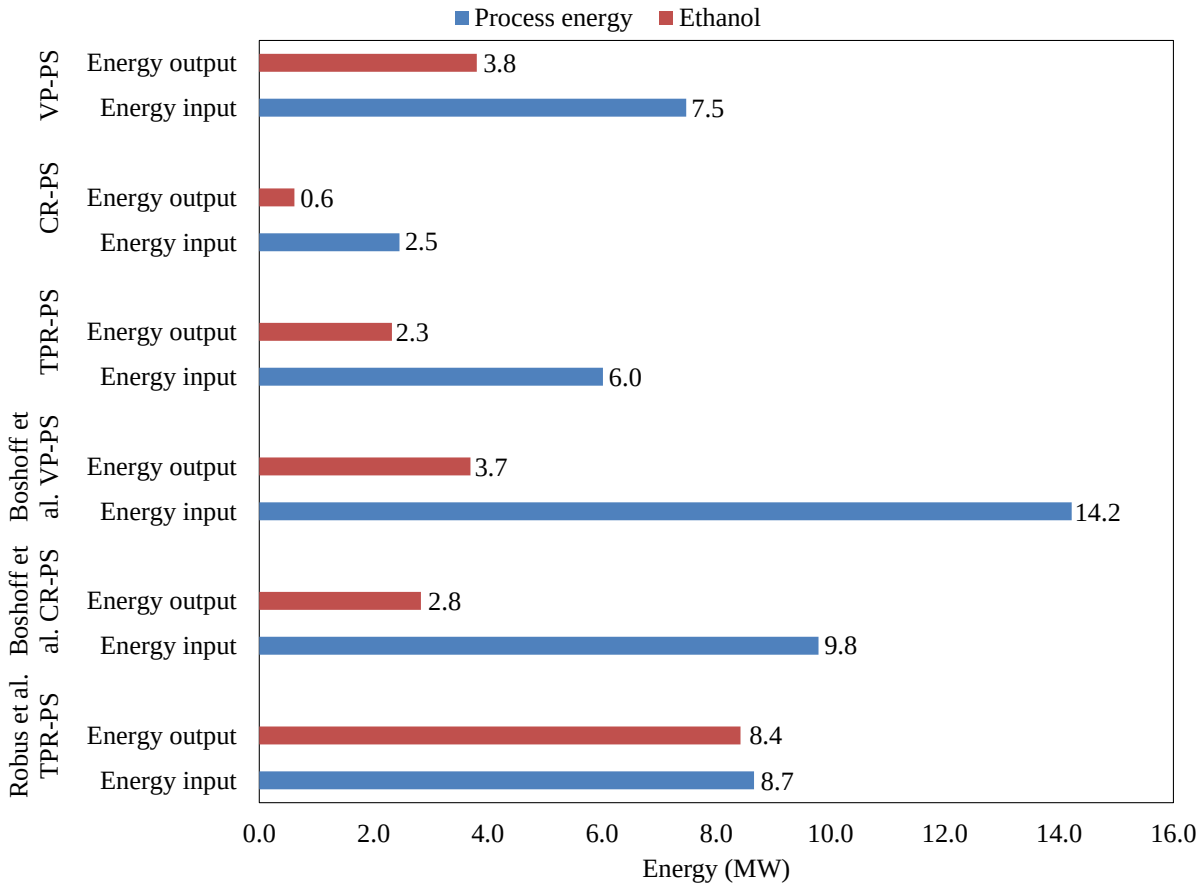

Figure 4-4: Comparison of energy input and biofuel output for fermentation

The lowest energy ratio was for VP-PS at 2.0, while TPR-PS and CR-PS had ratios of 2.6 and 4.0, respectively. These values indicate that more energy is needed to operate the process and produce the biofuel, than the amount of energy the biofuel can deliver.

The experimental results for paper sludge from similar mills reported by Robus et al. (2016) and Boshoff et al. (2016) were also modelled using the same simulation, with the results included in Figure 4-4. It can be seen that the TPR-PS studied by Robus et al. (2016) has an energy ratio of close to 1.0, however the fermentation model used in this study does not include the pre-treatment step of washing the paper sludge prior to fermentation described in the experimental method. The paper sludge used by Boshoff et al. (2016) have similar energy ratios (3.5 for CR-PS and 3.8 for VP-PS) to that of the VP-PS used in this study.

4.3.1.2 CAPEX & OPEX

From the mass and energy balance, the ethanol production per year was determined, indicated in Table 4-6, as well as the feedstock throughput per year and the ethanol yield. The highest yield is from VP- PS, at 112 L ethanol/dry tonne paper sludge, with almost double the yield of TPR-PS and CR-PS. This can be due to the high glucan content in VP-PS, as well as the low solids loading and high enzyme dosage, which increases the ethanol yield. Paper sludge with high bulk density and low water holding capacity also performed better, as discussed in Section 3.3.2. An additional scenario was created, where the yield of CR-PS was improved, on the basis of increasing the enzyme dosage from 11 FPU/g paper sludge to 20 FPU/g paper sludge, which is the same dosage that was used for VP-PS. It was assumed that the conversion would increase to a conservative estimate of 75%, which increases the yield from 60 to 68 L of ethanol/dry tonne paper sludge.

Table 4-6: Fermentation ethanol production results

	TPR-PS	**CR-PS**		**VP-PS**
		66% conversion	**75% conversion**	
Ethanol production (m3/year)	3180	840	960	5220
Feedstock production (wet tonne/year)	46310	14070	14070	46780
Yield (L ethanol/tonne PS)	70	60	68	112

The capital expenditure (CAPEX) and operating expenditure (OPEX) for each paper sludge is given in Figure 4-5. The CAPEX is comprised of the direct and indirect costs, as well as the working capital. The sum is equal to the total capital investment. The OPEX is comprised of the variable and fixed operating costs, which makes up the total operating cost per year (Humbird et al. 2016).

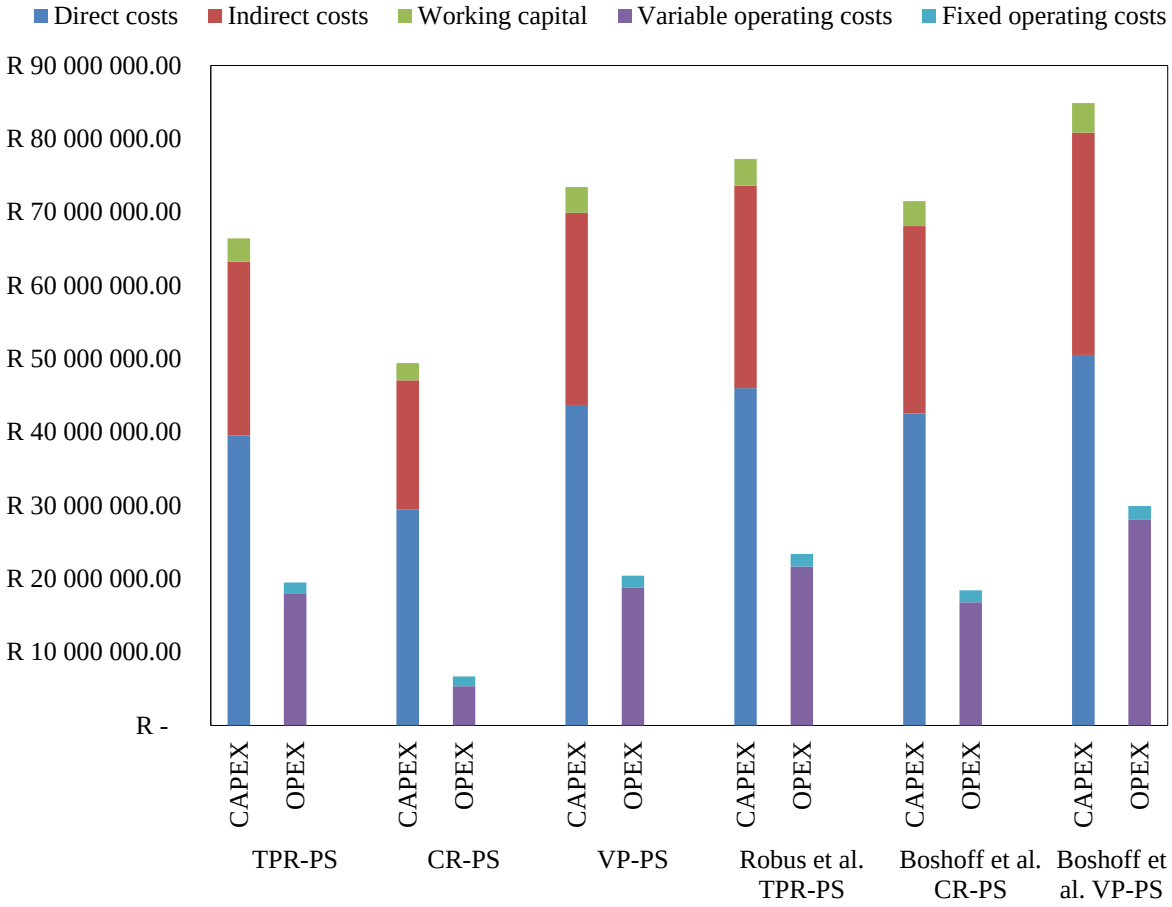

Figure 4-5: Capital and operating costs for fermentation

The total capital investment for TPR-PS, CR-PS (75% conversion) and VP-PS is R66 million, R49 million and R73 million, respectively. The higher capital costs are due to the higher throughput of paper sludge each day, which results in large equipment sizes and increased equipment costs. Similar capital costs (range of R33 million – R74 million, in 2012 Rand value) were found by Robus et al. (2016) when using vendor costs.

The total operating costs for TPR-PS, CR-PS (75% conversion) and VP-PS is R21 million, R8 million and R23 million, respectively. The cost of enzymes for 66% conversion of CR-PS is R0.71 per litre ethanol. At 75% conversion, the required operating cost of enzymes increases to R1.12 per litre ethanol. The increase in conversion due to the increased enzyme dosage results in the overall OPEX contribution of enzymes to increase from 12.9% to 21.1%. The operating costs are much higher for TPR-PS and VP-PS than for CR-PS due to the increased amount of paper sludge that needs to be processed. The fixed operating costs are relatively similar (in the range of R1.3 million to R1.7 million) for all paper sludge types. In comparison with the study conducted by Boshoff et al. (2016), slightly higher CAPEX is required for CR- PS and VP-PS.

4.3.1.3 Cash flow analysis

The minimum ethanol selling price (MESP) approach was taken, with the discount rate set at 12% which is 3% higher than the prime lending rate (Robus et al. 2016). The results are shown in Figure 4-6. The red line indicates the predicted ethanol selling price for 2016 which is at R8.39 per litre ethanol (Mandegari 2016).

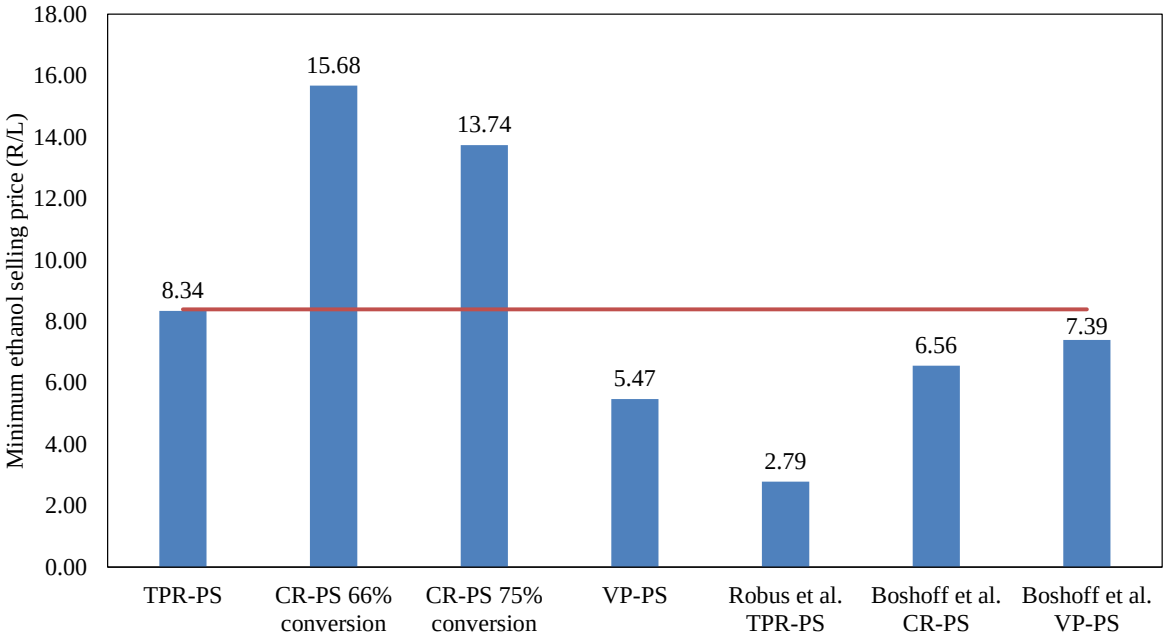

Figure 4-6: Minimum ethanol selling price with improved corrugated recycle conversion

TPR-PS and VP-PS fall under this threshold price, indicating it might be feasible if the ethanol selling price remains close to R8.39/L. The minimum selling price for CR-PS (66% conversion) is almost double the predicted selling price due to the low conversion of paper sludge. The second scenario with the conversion increased to 75%, results in an ethanol yield increase which increases the profit margin, and decreases the minimum ethanol selling price. The high CR-PS MESP is due to the very low paper sludge flow rates, which is less than 15 dry tonne/day. Fermentation processes only become economically feasible at flow rates above 30 dry tonne/day (Robus et al. 2016).

The cash flow analysis was completed using a second approach, where the selling price is fixed (at the ethanol selling price of R8.39/L) and the internal rate of return (IRR) can be determined by setting the NPV to zero. The IRR and payback period is shown in Figure 4-7. The IRR for TPR-PS, CR-PS (75% conversion) and VP-PS is 12.2%, 2.7% and 27.3%, with payback periods of 8, 20 and 4 years, respectively.

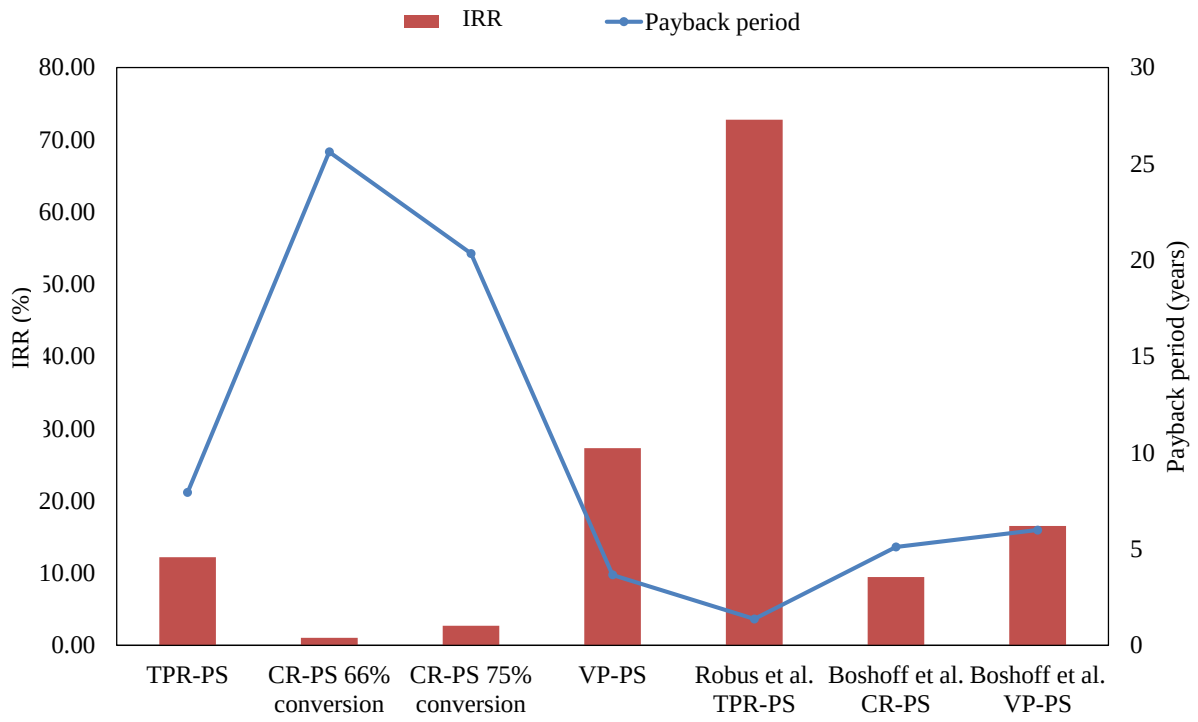

Figure 4-7: IRR and payback period for the fermentation process

4.3.1.4 Sensitivity analysis

A sensitivity analysis was done to investigate the effect that a change in a process parameter has on the minimum ethanol selling price. The total capital investment, electricity, steam, fresh water, transport and enzyme costs were varied by +/- 25% in order to see the effect on the MESP. The sensitivity analysis for TPR-PS can be seen in Figure 4-8. The total capital investment has the most pronounced effect, while fresh water and electricity price has very little effect. A decrease in the capital costs will improve the MESP, while steam and enzyme cost will also affect the MESP, it does not have as pronounced an effect as the capital investment.

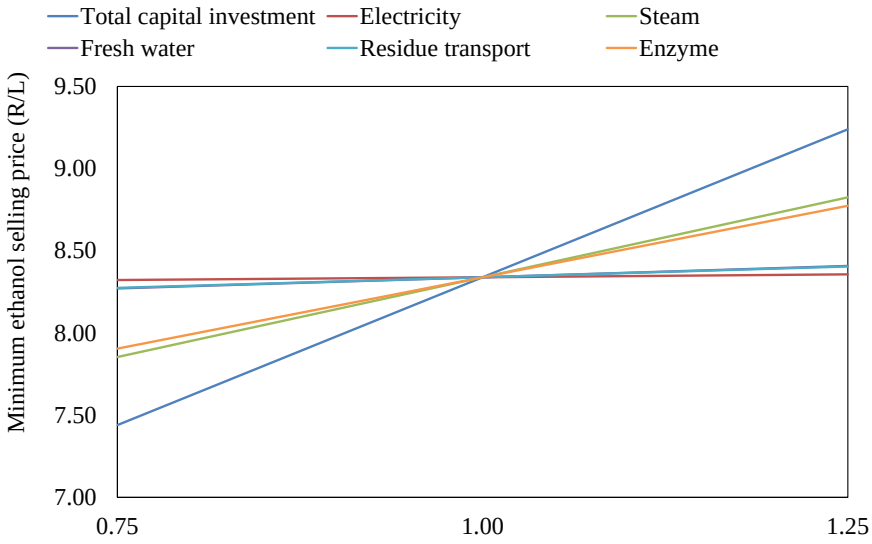

Figure 4-8: Sensitivity analysis for MESP for TPR-PS

The sensitivity analysis for CR-PS with 75% conversion is shown in Figure 4-9. The process is most sensitive to changes in the total capital investment, with less pronounced sensitivity to the steam cost. With a 25% decrease in capital investment costs, the MESP decreases to R11.52/L.

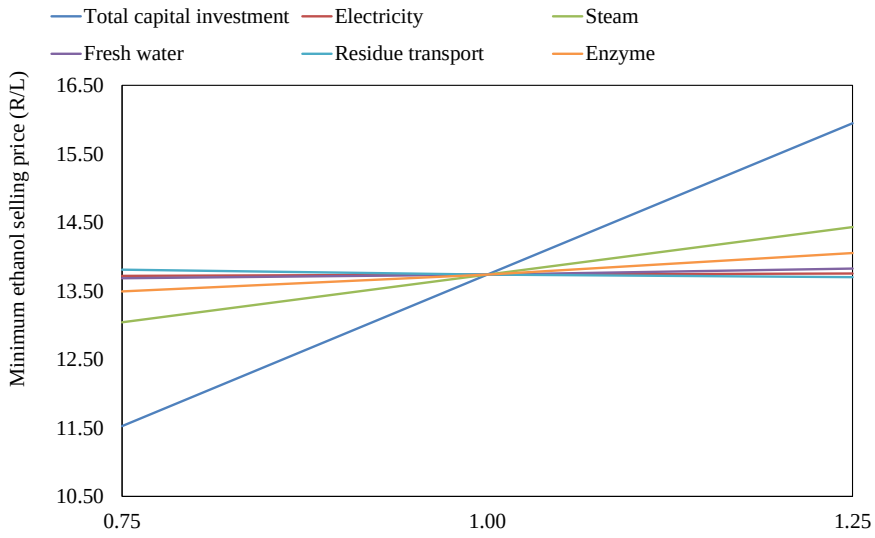

Figure 4-9: Sensitivity analysis for MESP for CR-PS

The sensitivity analysis for VP-PS is shown in Figure 4-10. The most sensitive parameter is the total capital investment, followed by the cost of steam. Less prominent parameters are enzyme cost and residue transport. Improvement in the screw steriliser design which uses the most steam, as discussed in Section 4.3.1.1, will further reduce the MESP of VP-PS, improving the fermentation route as most feasible bioprocessing solution.

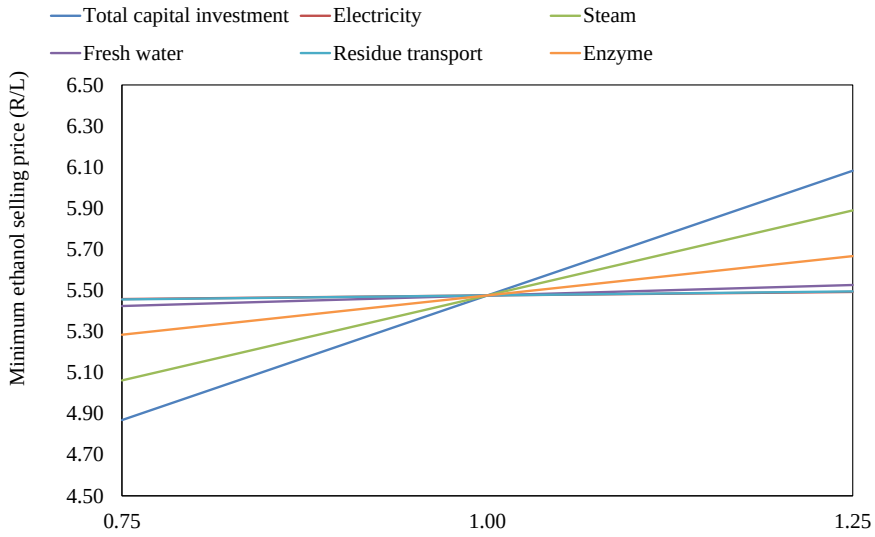

Figure 4-10: Sensitivity analysis for MESP for VP-PS

4.3.2 Anaerobic digestion techno-economic analysis

4.3.2.1 Energy balance and utility requirements

The energy balance comparing the process input energy and product output energy is shown in Figure 4-11. The energy ratios are better than those obtained during fermentation, discussed in Section 4.3.1.1, since the methane produced has more energy than the process energy needed to produce it. The respective energy ratios for TPR-PS, CR-PS and VP-PS are 0.5, 0.2 and 0.7. The highest energy requirement is the steam used to keep the temperature of the digester at 37°C for mesophilic anaerobes.

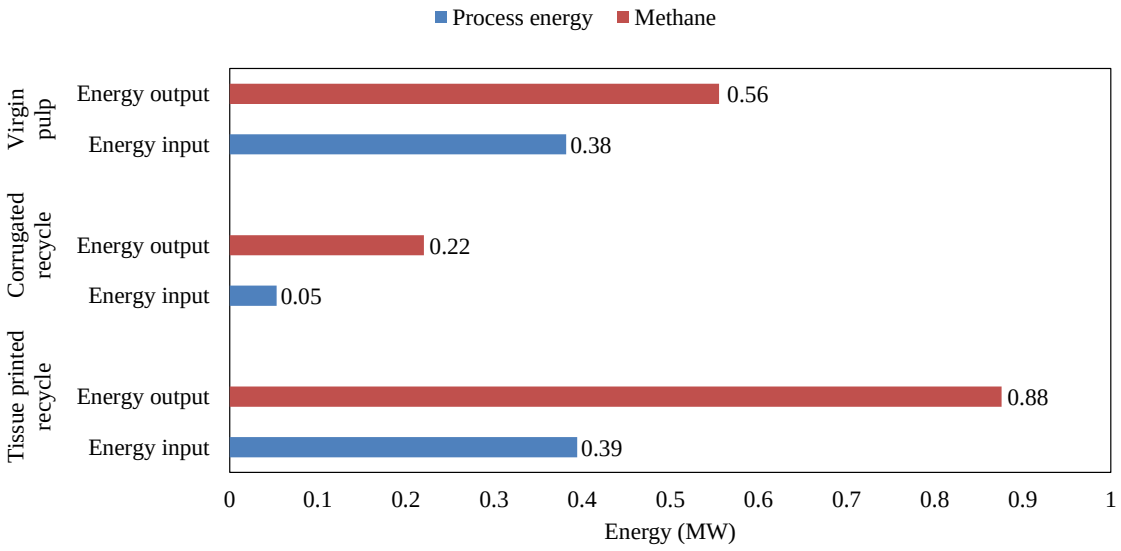

Figure 4-11: Comparison of energy input and output for anaerobic digestion

Although the energy balance looks promising, an in depth economic analysis needs to be done to take into account the capital expenditure as well as the operation costs, which will have an effect on the economic feasibility.

4.3.2.2 CAPEX & OPEX

The product yields were calculated in the Aspen Plus simulation, and are shown in Table 4-7. Despite CR-PS producing biogas with the highest methane content (58% v/v), the high paper sludge production rate of TPR-PS increases the methane production per year, which results in a higher methane yield. Even with the high production rate of VP-PS, similar to TPR-PS, the

lower methane content of the produced biogas and the low biogas production rates result in a methane yield of only 6.74 kg methane/tonne paper sludge.

Table 4-7: Anaerobic digestion methane production results

	TPR-PS	**CR-PS**	**VP-PS**
Methane production (kg/year)	498 000	125 000	315 000
Feedstock (wet tonne/year)	46 310	14 070	46 800
Yield (kg methane/tonne PS)	10.74	8.90	6.74

The CAPEX and OPEX for the anaerobic digestion process is shown in Figure 4-12. The total capital investment for TPR-PS, CR-PS and VP-PS is R196 million, R63 million and R189 million, respectively. The high capital cost is due to the digester being built from steel, as well as downstream upgrading of the biogas via a scrubber (New Horizon Energy, personal communication 2016). The low paper sludge production rate of CR-PS results in smaller equipment sizes and therefore reduces the cost of the equipment. The operating cost for TPR- PS is the highest, at R23 million, while CR-PS has the lowest operating cost of only R4 million. The operating cost comprises mainly of the variable operating cost, with the disposal of solid residues making up most of the variable operating costs.

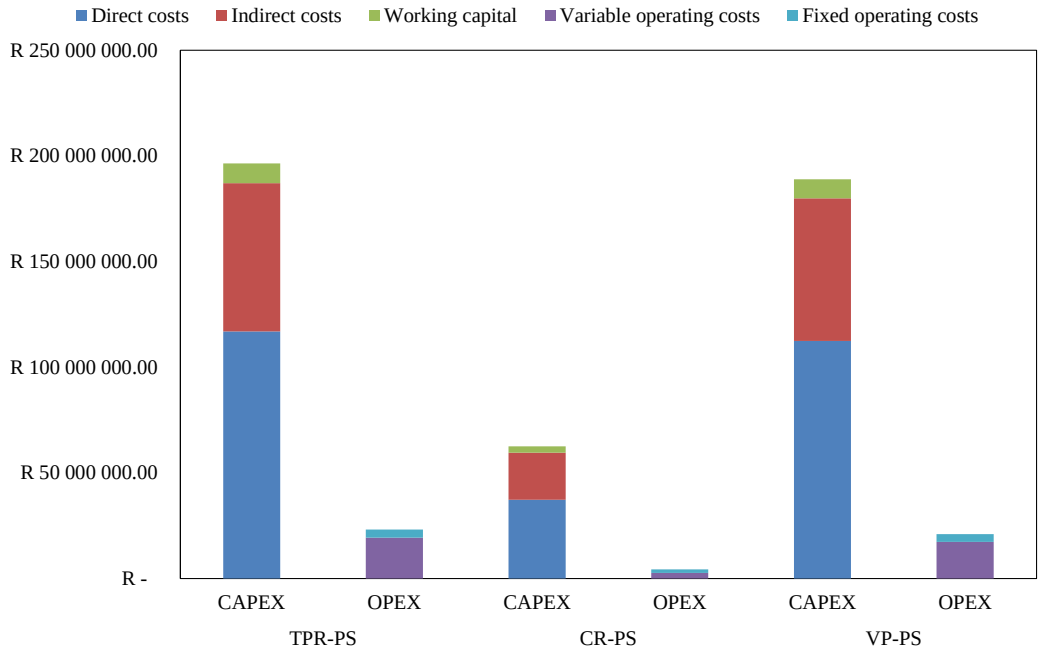

Figure 4-12: Capital and operating costs for anaerobic digestion

4.3.2.3 Cash flow analysis

The minimum methane selling price is shown in Figure 4-13. The minimum selling price was calculated at a fixed discount rate of 12%. The red line indicates the LPG energy equivalent price, calculated from the LPG selling price of R22.36/kg and HHV of 46.1 MJ/kg (Department of Energy Petroleum Products Acts, 2016). The energy equivalent price is R0.49/MJ. For methane the selling price is thus R27.26/kg.

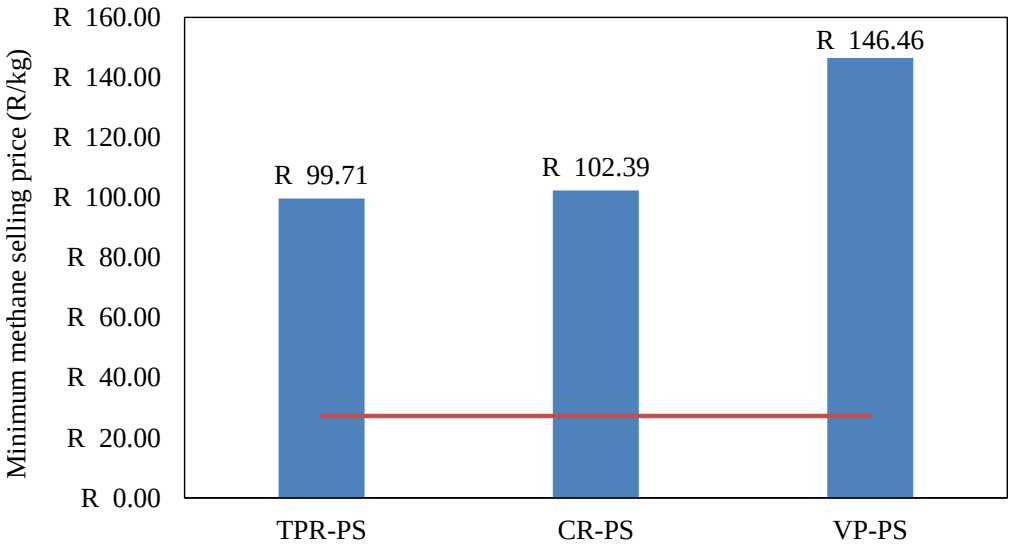

Figure 4-13: Minimum methane selling price

The lowest selling price is for TPR-PS at R99.71/kg, which is more than three times higher than the threshold price of R27.26/kg. The highest methane selling price is for VP-PS, due to the high capital and operating costs, but without the methane yield to recover the costs from, as indicated in Table 4-7.

4.3.2.4 Sensitivity analysis

The sensitivity of the anaerobic digestion process was investigated, by changing the parameters by +/- 25%. Total capital investment, electricity, steam, fresh water, and residue transport cost was varied in order to see the effect on the minimum methane selling price. The results of the analysis for TPR-PS can be seen in Figure 4-14.

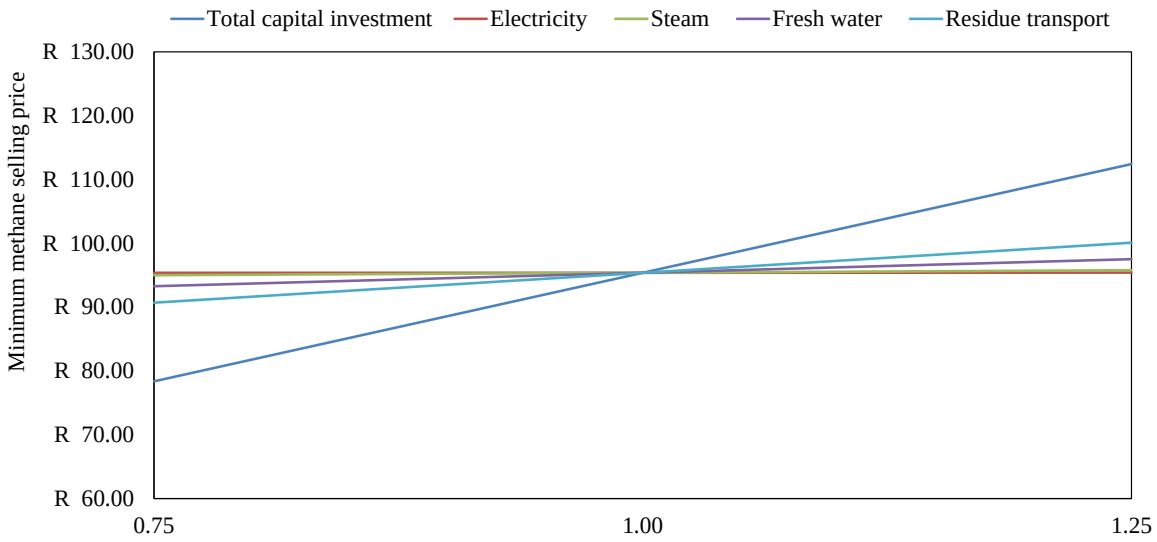

Figure 4-14: Sensitivity analysis for TPR-PS

The most pronounced change in methane selling price is when the capital investment is changed, with a 25% decrease resulting in selling price of less than R80/kg. However, this still does not bring the methane selling price close to the current market selling price. The sensitivity analyses for CR-PS and VP-PS showed similar results (not shown), with the minimum selling price showing the most prominent sensitivity to a change in the total capital investment.

4.4 Summary and conclusion

A techno-economic evaluation was done, investigating paper sludge that emanates from three different pulp and paper mills in South Africa. Two biochemical processing routes were studied, using experimental data from scaled up reactor experiments. Process flow diagrams were developed and used to simulate scenarios where all the paper sludge produced at the various mills were either fermented to produce bioethanol, or anaerobically digested to produce biomethane. These models were used in the costing process, to determine the operating and capital expenses, which are needed in the cash flow analysis.

From the cash flow analysis for fermentation, it can be concluded that virgin pulp paper sludge is the most feasible, due to the high paper sludge production rate which results in high ethanol yields. The minimum ethanol selling price is R5.47/L, which is well below the threshold ethanol selling price of R8.39/L. The internal rate of return is 27% with a payback period of 4 years. Low annual paper sludge production, as well as low ethanol yields negatively impacted the feasibility of CR-PS.

Anaerobic digestion is not a feasible biochemical processing route, with none of the paper sludge reaching the market selling price for methane. TPR-PS, the best performing paper sludge, has a minimum selling price of R99.71/kg which is almost four times higher than the methane energy equivalent price of R27.26/kg. The low methane yields achieved through digestion and the high capital costs make this process an unattractive biochemical processing option.

Key technical areas for process improvements include optimisation of all the energy balances, specifically over the energy intensive heat exchanger required to cool down the sterilised paper sludge prior to fermentation. Anaerobic digestion as processing route is unfeasible, largely due to the high capital costs for the infrastructure required. However, as this process becomes more mature, it is expected that the capital costs will also largely be reduced.

Chapter 5: Conclusions and recommendations

Paper sludge: potential, not problem

5.1 Conclusions

Paper sludge from three paper and pulp mills in South Africa were selected that represent the majority of paper products produced in this industry. From chemical compositional analyses, it was found that tissue printed recycle paper sludge had the highest ash content of 63% (w/w) and lowest glucan content, while virgin pulp paper sludge had the lowest ash content and the highest glucan content of 52% (w/w). Corrugated recycle paper sludge had the highest xylan, lignin and extractives fraction.

Fed-batch simultaneous saccharification and fermentation experiments were conducted in a bioreactor with a volume of 20 L, as scale up experiment from 5 L bioreactors. It was determined that tissue printed recycle paper sludge can achieve ethanol concentrations of only 27.8 g/L, and 70.6% conversion of the available sugars. Corrugated recycle paper sludge achieved a higher ethanol concentration of 39.4 g/L, despite the low conversion of only 65.7%. Virgin pulp paper sludge achieved the highest ethanol concentration and conversion, producing 46.8 g/L bioethanol and converting 87.4% of the available sugars. It was observed that factors such as low bulk density and high water holding capacity negatively affect the enzymatic hydrolysis during the fermentation reaction by hindering the enzymatic action.

Anaerobic digestion experiments were conducted in 30 L digesters, as scale up experiments from 100 ml biomethane potential tests. Corrugated recycle paper sludge produced the highest amount of methane, yielding 54.4 L/kg paper sludge added, which is attributed to the high methane content of the biogas produced (57.7% v/v). Tissue printed recycle paper sludge produced 31.6 L methane/kg paper sludge, with the biogas having a methane content of 50.2% v/v. The biogas produced with the lowest methane content is from virgin pulp paper sludge, producing biogas with only 44.3% v/v methane, and a total of 37.2 L methane/kg paper sludge. Paper sludge with high bulk density and low water holding capacity performed better, owing to adequate amounts of free water for anaerobe cell growth. The ash content of the paper sludge has no adverse effect during digestion, as is the problem during fermentations. This makes anaerobic digestion of paper sludge from tissue mills an attractive biochemical processing route.

A techno-economic analysis was completed to investigate how the experimental yields influenced key economic indicators such as the minimum fuel selling price. The respective bioethanol yields were calculated to be 80, 68 and 112 L ethanol/tonne paper sludge for tissue printed recycle paper sludge, corrugated recycle paper sludge and virgin pulp paper sludge. The capital investment needed to build a fermentation plant ranges from R49 million to R73 million. The minimum selling price of ethanol for the three paper sludge types is close to the bench mark predicted ethanol price of R8.39/L, indicating a mature technology. The best performing paper sludge is virgin pulp paper sludge, with a minimum ethanol selling price of only R5.47/L and a payback period of 4 years. This is due to the high ethanol yield, as well as economy of scale: this virgin pulp mill produces 36 dry tonne paper sludge per day.

On the other hand, for the anaerobic digestion plant, low biomethane yields were achieved of only 10.7, 8.9 and 6.7 kg methane/tonne paper sludge for tissue printed recycle paper sludge, corrugated recycle paper sludge and virgin pulp paper sludge. The capital investment for an anaerobic digestion plant ranges from R63 million to R196 million causing the minimum selling price of methane to be almost three fold more than the methane market price of R27.26/kg. The “best” performer is tissue printed recycle paper sludge, however the minimum methane selling price is R99.71/kg. A combination of low biomethane yield per tonne paper sludge, as well as high capital investment makes anaerobic digestion an unattractive processing route.

5.2 Recommendation for future research

5.2.1 Fermentation

It is recommended that the enzyme dosage be calculated based on a dosage of FPU/g glucan instead of FPU/g paper sludge. Since there is large variability within categories, this method will account for compositional differences, yet maintain the standard enzyme dosage rate. It is also recommended that the viscosity of the broth be tracked during the fermentation, in order to be able to conclude on how fed-batch feedings can best be done to reduce the viscosity of the broth. Another interesting optimisation study would be on the fed-batch feeding interval time and paper sludge batch size on the ethanol yields. An energy balance optimisation study can be performed, focussing principally on the reduction of the high energy demands during the sterilisation step prior to fermentation.

It has been suggested that the residues after the fermentation process can be used as feedstock for pyrolysis or anaerobic digestion, where economic evaluations of these processes can shed some light on their feasibility. The use of fermentation residues has been proven feasible for sugarcane bagasse (Liu et al. 2015) and for paper sludge (Kemppainen et al. 2012). During fermentation, the total mass decreases to approximately 30% of the original mass, which allows for significant reduction in disposal costs. However, if the fermentation residues are to be used in a downstream anaerobic digestion process, the size of the equipment needed will be significantly reduced, which will lower the total capital investment and increase the profit margin. In Chapter 4 it was seen that stand-alone anaerobic digestion is not feasible due to the high capital costs due to large digester sizes, but with the above mentioned reduction in feedstock volumes, a more feasible solution would be a combined fermentation-digestion process.

5.2.2 Anaerobic digestion

An improvement in the current design of the digesters could result in better characterisation and understanding of the digestion process. The current impellers could be replaced with similar impellers as described by Liao & Li (2015). Better mixing will allow better heat transfer between the jacket and the vessel, allowing for better stability of the digestion process. Feedstock properties, such as the C:N ratio and digestibility can also be investigated, which will improve the biogas product quality.

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