

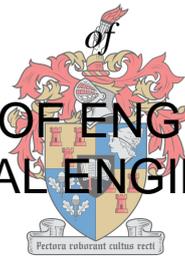
Application of membrane technology for purifying tyre derived oil

by

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Declaration

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Abstract

Tyre derived oil (TDO) is an abundant liquid product obtained after pyrolysis of waste tyre. It contains a complex mixture of C₆–C₂₄ organic compounds of various classes such as paraffins, olefins, aromatics, nitrogen and sulphur compounds as well as oxygenated compounds. TDO is a potential source of high market value compounds such as *dl*-limonene, 4-vinylcyclohexene, toluene, ethylbenzene, xylenes and many others. *dl*-limonene is the most abundant valuable chemical in TDO. Valuable chemicals in TDO are only marketable at purities greater than 90% v/v. *dl*-limonene together with p-Cymene, indane and 1,2,4-trimethylbenzene have similar physical properties such as boiling point and viscosity. Conventional distillation procedures fail to purify limonene from TDO because of these limonene-like impurities.

TDO is also a potential fuel for diesel engines. The calorific value of TDO has been reported to be approximately equal to that of commercial fuels. Other commercial fuel properties that match that of TDO include flash point, density, viscosity etc. For fuels, the South African national standards (SANS) specifies that fuels must contain a sulphur content of less than 500 ppm. Benzothiazole is reportedly the most abundant sulphur species in TDO. The purification of limonene and the reduction of benzothiazole from TDO is vital in the field of waste tyre valorisation.

The aim of this study is to investigate the purification (recovery of limonene and reduction of benzothiazole) of TDO using a novel green separation technology, namely organic solvent nanofiltration (OSN). OSN allows size-exclusion based separation with the absence of phase transitions to ensure much lower energy consumption and therefore a favourable economic and carbon footprint compared to the conventional separation methods such as distillation.

Three different commercial OSN membranes, Puramem®-280 (PM-280), STARMEM™-280 (ST-228) and Duramem®-200 (DM-200), were employed for the experimental work of this study. TDO was allowed to permeate through a membrane installed to a dead-end OSN set-up. The transmembrane pressure (10-40 bar), species concentration (50-150 ppm) and feed dilution (toluene, 1-octene and ethanol) were all varied so as to investigate the effect on membrane performance (flux and rejection).

It was found that pure species (Limonene, p-Cymene, 1,2,4-trimethylbenzene and toluene) permeate at distant rates through PM-280 relative to ST-228 and DM-200. The distant rates through PM-280 imply that the membrane is more selective than ST-228 and DM-200. Flux of pure species through PM-280 (30 bar) ranged from 75 L.m⁻².h⁻¹ to 297 L.m⁻².h⁻¹. Pure species flux was found to be highly dependent on transmembrane pressure, molecular weight and parameters describing the interaction between the membrane and the pure species. It was found that pure benzothiazole destroys the membrane surface of both PM-280 and ST-228.

The purification of TDO through PM-280 and ST-228 resulted in high TDO rejections, 88% and 100% respectively. Concentration polarization was deduced as a possible explanation for the high TDO rejections. Negative rejections were recorded with PM-280 for limonene and benzothiazole, -6% and -7% respectively. Negative rejections imply that the species is more concentrated in the permeate than in the feed solution. For this study, a negative rejection is a good performance by the membrane since it implies that the targeted compounds are being drawn out of the crude TDO.

As an effort of enhancing membrane performance, TDO was diluted with different solvents (toluene, 1-octene and ethanol). TDO/toluene dilution enhanced the membrane performance by resulting in higher negative rejections through ST-228, -10% and -98% for limonene and benzothiazole respectively. The membrane performance was still not competent since benzothiazole percent change was only 6.3%. However, it was found that the transport of diluted TDO species across the membrane is highly influenced by the interaction between the membrane and the species. A species having a strong affinity for the membrane recorded a low rejection compared to a species having a weak affinity for the membrane.

It was also found that the membrane performance is unaffected by the concentration of TDO species. The technical-viability of OSN in purifying or fractionating crude TDO is unnoticed in this study.

Through comparison, it was noticed that the breakthrough for TDO sulphur reduction and limonene recovery is likely to happen through distillation procedures.

Opsomming

Band afkomstige olie (BAO) is 'n oorvloedig verkrygbare vloeistofproduk afkomstig vanuit die pirolise van afval voertuigbande. Dit bevat 'n komplekse mengsel van C₆-C₂₄ organiese verbindings van verskeie klasse soos paraffiene, olefiene, aromatiëse verbindings, stikstof- en swael-bevattende verbindings sowel as geoksigineerde verbindings. BAO is 'n potensiële bron van hoë markwaarde verbindings soos *dl*-limonien, 4-vinielsikloheksen, toluen, etielbensen, xileen, en baie ander. *dl*-Limonien is die waardevolste verbinding in BAO. Waardevolle chemikalieë in BAO is slegs bemerkbaar in suiwerheidsgrade groter as 90% v/v. *dl*-Limonien, tesame met *p*-cymien, indaan en 1,2,4-trimetielbensen het soortgelyke fisiese eienskappe soos kookpunt en viskositeit. Konvensionele distillasie prosedures is nie in staat om limonien te suiwer uit BAO nie weens die teenwoordigheid van hierdie limonien-soortgelyke onsuiverhede.

BAO is ook potensieel 'n brandstof vir dieselenjins. Die kalorifiese waarde van BAO is al beskryf as ongeveer gelykstaande aan dié van kommersiële brandstowwe. Ander kommersiële brandstofeienskappe wat soortgelyk is aan dié van BAO sluit in vlampunt, digtheid, viskositeit, ens. Die Suid-Afrikaanse nasionale standaard (SANS) spesifiseer dat brandstowwe 'n swaelinhoud van minder as 500 ppm moet hê. Bensotiasool word algemeen gerapporteer as die volopste swaelspesie in BAO. Die suiwing van limonien vanuit BAO en die verlaging van bensotiasool in BAO is noodsaaklik in die veld van band valorisasie.

Die doel van hierdie studie is die suiwing (herwinning van limonien en verlaging van bensotiasool) van BAO deur gebruik te maak van 'n nuwe, groen, omgewingsvriendelike tegnologie, naamlik organiese oplosmiddel nanofiltrasie (OON). OON maak grootte-uitsluitingsgebaseerde skeiding in die afwesigheid van fase oorgange moontlik, om sodoende heelwat laer energieverbruik te verseker. Derhalwe word 'n meer gunstige ekonomiese en koolstofvoetspoor verkry in vergelyking met die konvensionele skeidingsmetodes soos distillasie.

Drie verskillende kommersiële OON membrane, Puramem®-280 (PM-280), STARMEM™-280 (ST-228) en Duramem®-200 (DM-200), is gebruik vir die eksperimentele werk in hierdie studie. BAO is toegelaat om deur 'n membraan te dring wat aan 'n doodlopende OON opstelling geïnstalleer is. Die transmembraan druk (10-40 bar), chemiese spesie konsentrasie (50-150 ppm) en oplosmiddeltipe (tolueen, 1-okteen en etanol) is gevarieer om die effek op membraan werksverrigting (vloed en uitskotverlies) te ondersoek.

Daar is gevind dat suiwer chemiese spesies (limonien, *p*-cymien, 1,2,4-trimetielbensen en toluen) teen duidelik verskillende tempo's deur PM-280 dring in vergelyking met hul bewegingstempo's deur ST-228 en DM-200. Hierdie groot verskil in deurdringingstempo in die geval van PM-280 impliseer dat die membraan meer selektief is as ST-228 en DM-200. Die vloed van suiwer chemiese spesies

deur PM-280 (30 bar) het gevarieer van $75 \text{ L.m}^{-2}.\text{h}^{-1}$ tot $297 \text{ L.m}^{-2}.\text{h}^{-1}$. Daar is bevind dat 'n suiwer spesie se vloed deur 'n membraan hoogs afhanklik is van transmembraan druk, molekulêre gewig en parameters wat die interaksie tussen die membraan en die suiwer spesie beskryf. Daar is ook gevind dat suiwer bensotiasool die membraanoppervlak van beide PM-280 en ST-228 vernietig het.

Die suiwering van BAO deur PM-280 en ST-228 het gelei tot hoë BAO uitskotverliese van 88% en 100%, onderskeidelik. Konsentrasie polarisasie kan voorgestel word as 'n moontlike verklaring vir die hoë BAO verliese. Negatiewe verliese, van -6% en -7%, is aangeteken met PM-280 vir limonien en bensotiasool, onderskeidelik. Negatiewe verliese impliseer dat die spesie meer gekonsentreerd is in die deurloop oplossing as in die toevoeroplossing. Vir hierdie studie beteken 'n negatiewe verlies 'n goeie werksverrigting by die membraan aangesien dit impliseer dat die teikenverbindings vanuit die ru BAO onttrek word.

In 'n poging om die membraan werksverrigting te bevorder, is die BAO verdun met verskillende oplosmiddels (tolueen, 1-okteen en etanol). BAO/tolueen verdunning het die membraan se werksverrigting verbeter deurdat dit gelei het tot hoër negatiewe verliese deur ST-228, met onderskeidelik -10% en -98% vir limonien en bensotiasool. Die membraan se werksverrigting was egter steeds nie aanvaarbaar nie aangesien die bensotiasool persentasie verandering slegs 6.3% was. Daar is egter gevind dat die vervoer van 'n verdunde BAO spesie oor die membraan baie beïnvloed is deur die interaksie tussen die membraan en die chemiese spesie. 'n Spesie met 'n sterk affiniteit vir die membraan het 'n lae uitskotverlies getoon in vergelyking met 'n spesie wat 'n swak affiniteit vir die membraan het.

Daar is ook gevind dat die membraan se werksverrigting nie beïnvloed is deur die konsentrasie van die BAO spesies nie. Die tegniese lewensvatbaarheid van OON vir die suiwering of fraksionering van ru BAO is nie waargeneem in hierdie studie nie.

Deur vergelyking is waargeneem dat die deurbraak vir BAO swaelvermindering en limonien herwinning waarskynlik sal geskied deur distillasie prosedures.

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Dedication

I would like to dedicate this work to the inspiring lives of my late uncle and aunt:

Bishop SE Tshindane

&

Mrs SS Tshindane.

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List of abbreviation

BTX	Benzene, Toluene and Xylenes
C _n	Carbon number
DCM	Dichloromethane
DM	Duramem®
GC	Gas Chromatography
GC-FID	Gas Chromatography-Flame ionization detector
GC-MS	Gas Chromatography-Mass spectrometry
IS	Internal standard
MET	Membrane extraction technology
MF	Microfiltration
MWCO	Molecular weight cut-off
NF	Nanofiltration
NR	Natural rubber
OSN	Organic Solvent Nanofiltration
PA	Polyamide
PAN	Polyacrylonitrile
PAH	Polycyclic aromatic hydrocarbon
PB	Polybutadiene
PDMS	Polydimethylsiloxane
PI	Polyimide
PVA	Polyvinyl alcohol
PM	Puramem®
PVDF	Polyvinylidene fluoride
REDISA	Recycling and Economic Development Initiative of South Africa
RO	Reverse Osmosis
SANS	South African National Standards
SBR	Styrene-Butadiene Rubber
SO _x	Sulphur Oxides
ST	STARMEM™
TDO	Tyre derived oil
UF	Ultrafiltration
WT	Waste tyre

List of Symbols

A	Mass active area	m ²
C _f	Feed concentration	mg/L
C _p	Permeate concentration	mg/L
E _v	Energy of vaporization	Cal/mol
J	Volume flux	L.m ⁻² .h ⁻¹
L _p	Membrane permeance	L.m ⁻² .h ⁻¹ .bar ⁻¹
M	Mass	Kg
MW	Molecular weight	g/mol
P	Pressure	Bar
R	Rejection	%
rpm	Rotations per minute	-
Δt	Time difference	Minutes
V	Volume	ml
V _m	Molar volume	m ³ /mol
δ _i	Solubility parameter of species i	MPa ^{0.5}
δ _{p84}	Solubility parameter of membrane	MPa ^{0.5}

CHAPTER 1

Introduction

1.1 Background and motivation

The quantity of waste tyres is significantly increasing as a result of the rapid development of the transport industry and the non-biodegradability of tyre material (Ahmad and Ahmad, 2013; Wei *et al.*, 2016; Dung *et al.*, 2009). Researchers (Zhang *et al.*, 2016; Dung *et al.*, 2009) reported that approximately 1.4 billion waste tyres are being disposed annually worldwide, corresponding to an estimated 17 million tons of waste tyres each year. In South Africa (Gosling, 2015), it is estimated that approximately 60 million to 100 million waste tyres are stockpiled across the country and 11 million waste tyres are being added to the pile every year. Majority of these waste tyres are disposed in open dumps and landfill sites resulting in environmental hazards such as uncontrollable fires, pollution of the atmosphere, contamination of soil and underground water and providing ideal breeding grounds for disease carrying mosquitoes (Wei *et al.*, 2016; Danon *et al.*, 2015; Blackman and Palma, 2002). In South Africa and other parts of the world, waste tyres are also burnt for their scrap metal content, emitting lots of toxic substances and black smoke, particularly dioxins and carbon monoxide that pollute the air (Gosling, 2015).

The recycling and economic development initiative of South Africa (REDISA) is a sustainable national tyre recycling organization that cooperates with research facilities across the country to develop methods of valorising waste tyre (Gosling, 2015). The project at hand falls within the REDISA scope.

Waste tyre management has become a global task that aims to valorise and recycle waste tyres. Metal and plastic can be simply recycled by melting to obtain the raw materials necessary for building new products. Raw materials in waste tyre are not directly recyclable because of the complex structure of vulcanized rubber used during tyre fabrication. Devulcanization or a suitable degradation process is required for regeneration or recovery of raw materials in tyres (Karaagac *et al.*, 2015). Rubber reclaiming, pyrolysis, gasification and liquefaction have become some of the many possible ways of overcoming the problem of tyre disposal. Pyrolysis of waste tyre is the most employed method of recycling waste tyre (Zhang *et al.*, 2016; Ayanoglu and Yumrutas, 2016).

Pyrolysis is the thermal degradation of organic matter in the absence of oxygen at typical temperatures to produce oil, gas and char as pyrolytic products (Hita *et al.*, 2016; Williams, 2013). Pyrolysis of waste tyres is currently receiving the most interest as a route to disposal and valorisation of large quantities of waste tyres throughout the world (Williams and Taylor, 1993). Advantages of waste tyre pyrolysis range from the many applications of its products. For example, tyre derived oil (TDO) can be used directly as a fuel because of its high calorific value (43 MJ/kg) and other properties similar to that of diesel and gasoline. TDO can also be used as a potential source of refined valuable chemicals (Cunliffe and Williams, 1998). TDO is the most abundant and most investigated of all pyrolysis products with a dark brown colour and a strong acrid odour (Nkosi and Muzenda,

2014; Hita *et al.*, 2016). TDO contains valuable aromatic, aliphatic and terpene compounds such as BTX (Benzene, Toluene, and Xylene), *dl*-limonene, etc. (Wei *et al.*, 2016; Nkosi and Muzenda, 2014). In addition to the chemical composition of TDO, hetero-aromatic substances such as sulphur containing compounds have been reported to be present in TDO (Murillo *et al.*, 2006).

Extraction of valuable compounds such as limonene and reducing sulphur content in TDO has become an attractive and challenging area of research (Danon *et al.*, 2015). Conventional purification techniques such as distillation have been applied by researchers (Stanciulescu and Ikura, 2006; Roy, 1993) to purify TDO and to isolate valuable compounds. Due to the complex chemical composition of TDO, compound extraction by ordinary distillation results in a fraction of chemicals of the same boiling point. The addition of an entrainer that will shift the boiling point of the targeted compound in the TDO fraction has become a popular method of compound extraction by distillation (Stanciulescu and Ikura, 2006). Distillation is well known for high consumption of energy since it involves phase inversion of liquid to gas. Addition of an entrainer for extracting valuable compounds makes TDO purification by distillation more costly and complex (Danon *et al.*, 2015; Nazim *et al.*, 2014).

One interesting technique known for energy efficiency, greener operations and quality performances is membrane technology (Szekely *et al.*, 2014; Stoller *et al.*, 2016). Membrane technology is applied in various chemical industries for different purposes such as recovery of catalysts, biodiesel production, dewaxing of lube oil, purification of organic solvents, fractionation of hydrocarbon oils etc. (Priske *et al.*, 2015; Solomon *et al.*, 2014). Separation through a membrane depends on various properties such as molecular weight, geometry, viscosity, polarity, and charge (Cho *et al.*, 2000). Recent advances on membrane separations have led to the development of Organic Solvent Nanofiltration (OSN), regulating the concern of long-term stability of membranes in non-aqueous solutions. OSN is a pressure driven technique that offers nanoscale separations in non-aqueous mediums (Soltane *et al.*, 2016). The basic principle of OSN explains that molecules with a size larger than the nanopore section of the active layer will not pass through the membrane while smaller molecules permeate through (Szekely *et al.*, 2014; Volkov *et al.*, 2008).

An elaborate search of relevant literature yielded no publication of TDO purification/fractionation by a membrane. However, membranes have been feasibly applied for purifying other types of oil. One interesting type of oil is the oily waste water from chemical industries. Oily waste water has a similar complex chemical composition as TDO. An oily waste water purification study (Blistad and Espedal, 1996) reported that ultrafiltration membranes can retain 96% of the total hydrocarbon concentration and 54% of BTX in oily wastewater. Membranes have also been successfully applied to recover glycerols, triglycerides, monoglycerides, diglycerides and phospholipids from vegetable oils (Desai *et al.*, 2002). Researchers (Werth *et al.*, 2017) have reported that OSN processes in oleochemical industries can reduce energy demands by more than 70%.

The study at hand aims to utilize OSN membranes which are known to have smaller pores and better chemical stability. The chemical stability enables membranes to maintain their original structure and separation characteristics for long during operation.

1.2 Aim and objectives

The aim of this study is to investigate the possible technical viability of using OSN in fractionating or purifying TDO. The aim of this study will be achieved by completing the following objectives:

Objective 1: TDO characterisation

- Describe the chemical composition and other relevant properties of TDO.

Objective 2: OSN membrane separation performance

- Screen different commercial OSN membranes for pure species flux and compatibility with TDO.
- Characterise the OSN membranes in terms of TDO flux and species rejection.
- Evaluate the effect of pressure, species concentration and TDO dilution on the overall membrane performance.

Objective 3: Performance of OSN and conventional techniques

- Comparison between TDO purification by OSN and conventional techniques.

1.3 Scope and layout of thesis

Figure 1.1 summarises the scope of this investigation in a form of a flow chart. This project aims to investigate the feasibility of purifying TDO using OSN membranes. This thesis is subdivided into five chapters of relevant context necessary to achieve the objectives listed in Section 1.2.

Chapter 2 is a complete theoretical background that offers detailed information to all the concepts and terminologies related to TDO and OSN. The TDO chemical composition is discussed followed by the principles and success of OSN from previous publications. This chapter was constructed with an effort of understanding OSN processes and important concepts necessary to achieve the aim of this study.

Chapter 3 describes in detail all the experimental and analytical methodologies used in this study.

Chapter 4 presents the results obtained regarding the screening of available OSN membranes and the evaluation of OSN membranes in terms of TDO flux and species rejection. Section 4.5 presents the comparison between TDO purification by OSN and TDO purification by distillation and other conventional separation techniques.

Chapter 5 presents the main conclusions reached by this study. Recommendations for future work in TDO purification by membranes are also presented.

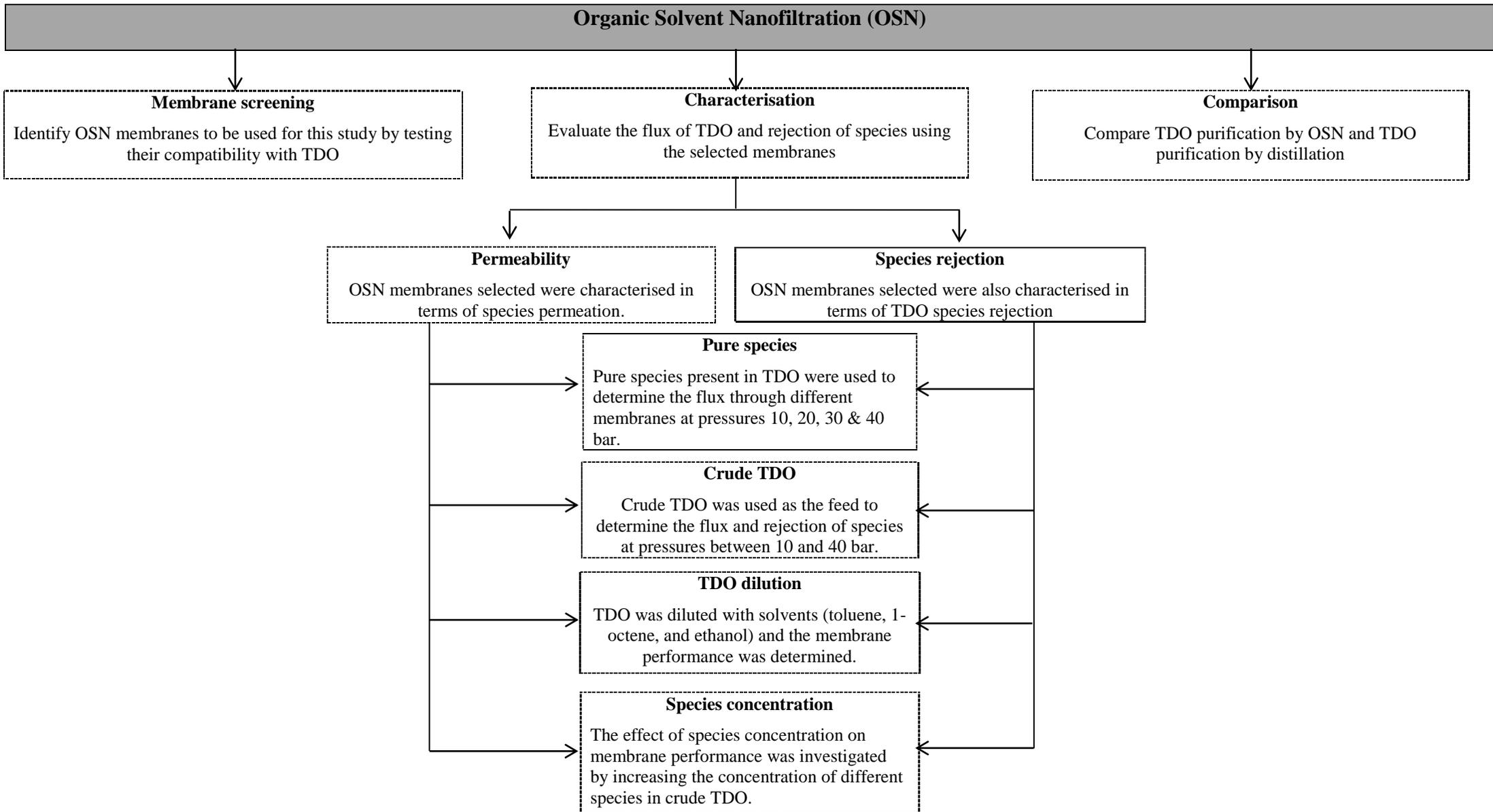


Figure 1.1: Scope of the project

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CHAPTER 2

Literature Review

2.1 Overview

Chapter 2 provides a theoretical foundation necessary to explain and understand experimental work and all results of this investigation. Different terminologies, principles and literature survey relevant to this study are presented. The opening section (Section 2.2) focuses on waste tyre recycling through pyrolysis. Section 2.3 presents the TDO chemical composition and applications of some valuable chemicals found in TDO. Sub-sections of Section 2.3 present the formation of limonene in TDO, formation of aromatics and polycyclic aromatic hydrocarbons (PAH) and the formation of hetero-aromatic compounds. Section 2.4 discusses the traditional methods of purifying TDO and recovering valuable species. Section 2.4 also includes all challenges and alternatives that present researchers encounter and introduce when purifying TDO. In Section 2.5, focus is shifted to OSN and all membrane related concepts that are necessary for this study. The opening part of Section 2.5 is a general introduction of OSN followed by principles and a review of the previous work done concerning the processing of oils by membranes.

2.2 Recycling of waste tyres

Waste tyres contain fibres, steel belts and tread rubber as the three main components (Al-Aqeeli, 2015). In South Africa, millions of waste tyres are lying in dumps and landfill sites. REDISA reported that approximately 11 million waste tyres are added to the existing pile every year. On an international scale, it is reported that 1.4 billion waste tyres are disposed in dumps annually (Zhang *et al.*, 2016; Dung *et al.*, 2009).

Waste tyre cannot be simply dumped on landfill sites and open spaces due to the implications they bring to the environment and human health. Unlike other materials, waste tyres are not easily degradable by soil due to the presence of disulphide bonds (R-S-S-R) responsible for linking rubber materials. Waste tyres dumped on landfill sites contribute to the spread of various diseases (e.g. malaria) by becoming breeding grounds for mosquitoes and bacteria. Burning of waste tyre is also a commonly used method of waste tyre disposal resulting in the emission of toxic gases such as sulphur dioxides to the atmosphere. The environmental challenges introduced by the irresponsible disposal of waste tyres calls for better ways of waste tyre management.

Tyre is fabricated by rubber materials of polybutadiene (PB), styrene-butadiene (SBR) and natural rubber (NR). In addition to polymeric materials in tyre, carbon black, steel, fibrous materials and vulcanising agents are added during tyre fabrication (Kwon *et al.*, 2015). The rubber material of a waste tyre is still valuable and can be recycled into new tyres. Karaagac *et al.* (2015) suggested that a suitable devulcanization (removal of disulphide bonds) process is required for recycling the rubber material in waste tyre. The recycling of waste tyre begins with the separation of rubber material from steel belts and fibrous materials. Pyrolysis has become the most common way of recycling waste tyre and other rubber containing materials.

2.2.1 Pyrolysis

Pyrolysis is defined as the thermochemical decomposition/break-down of organic matter at high temperatures (400°C - 900°C) in the absence of oxygen (Bridgwater *et al.*, 1999; Hita *et al.*, 2016). In North America, waste tyres are being recycled through pyrolysis to avoid site dumping and burning (Banipal and Mullins, 2001). In South Africa the number of waste tyre pyrolysis plants is still low. The waste tyre pyrolysis plants currently available in South Africa are; Milvinetix (Pty) Ltd, Metsa (Pty) Ltd and Premium green fuel (Pty) Ltd. The advantage of recycling waste tyre through pyrolysis lies in the generation of valuable products from waste.

During pyrolysis of waste tyre, the volatile organic part of the tyre (SBR, NR and PB) is converted to gases and liquids that have many applications in the fuel and chemical refining industry. The inorganic components (steel) and non-volatile carbon black remain as a solid residue (char) (Laresgoiti *et al.*, 2004; Banar *et al.*, 2012; Susa and Haydary, 2013). Each of the three products formed (gas, oil and char) has a broad range of applications (Hita *et al.*, 2016). For a typical waste tyre pyrolysis process, the products are 55% oil, 6% gas, 25% carbon black and 14% steel and fibres (Roy *et al.*, 1990; Roy *et al.*, 1995). Serio *et al.* (1992) also reported the same product distribution of 38-55 wt% oil, 33-38 wt% char and 10-30 wt% gas. The produced oil is referred to as pyrolytic oil/tyre pyrolysis oil/tyre derived oil. The tyre derived oil (TDO) name is the most preferred for this study.

TDO is the most abundant and most investigated of all the waste tyre pyrolysis products. TDO attracts researchers because of its ability to operate as a fuel for diesel engines. The fuel properties of TDO have been previously studied by researchers (Lopez *et al.*, 2011; Frigo *et al.*, 2014). The calorific value, flash point, density, viscosity and ultimate analyses were found to be similar to those of commercial fuels. The sulphur content (1.0 to 1.4 wt%) in TDO is high compared to other fuels (Susa and Haydary, 2013; Olazar *et al.*, 2008). Fuels with high sulphur content are not proper for using directly in diesel engines as they emit tons of toxic gases such as SO_x into the atmosphere.

Valuable chemicals such as *dl*-limonene are abundant in TDO (Susa and Haydary, 2013; Lopez *et al.*, 2011). The high concentration of valuable chemicals in TDO also attracts researchers into the field of waste tyre pyrolysis. TDO can be used as a chemical feedstock for valuable chemicals. Purification of TDO is necessary to reduce the sulphur content and to recover valuable chemicals.

2.3 TDO chemical composition

TDO is a very complex mixture of C_5 - C_{24} organic compounds of various chemical classes such as alkanes, aromatics, terpenes, polycyclic aromatic hydrocarbons (PAHs) as well as hetero-aromatic compounds (Frigo *et al.*, 2014). A TDO chemical composition of 42.1 wt% aromatics, 26.8 wt% alkanes, 26.6 wt% non-hydrocarbons and 4.1 wt% asphalt was reported by Dai *et al.* (2001). Conesa

et al. (1996) also reported a composition of 19.1 wt% aromatics, 21.3 wt% hetero-aromatics, 39.5 wt% aliphatics and 20.1 wt% polar fractions. The TDO chemical composition is dependent on pyrolysis parameters such as temperature, heating rate, presence of a catalyst, type of reactor, etc. Temperature is the most important (Banar *et al.*, 2012; Laresgoiti *et al.*, 2004). At high temperatures (> 500°C), compounds such as limonene degrade to form aromatic compounds such p-Cymene and trimethylbenzene.

Limonene and aromatics such as BTX and ethylbenzenes are some of the compounds considered valuable in TDO (Namchot and Jitkarnka, 2016). For example, toluene has a wide range of applications as a chemical feedstock and in the production of pesticides, surfactants and solvents (Cunliffe and Williams, 1998). Styrene which is also present in TDO has important applications in the production of plastic materials. The high concentration and high market value of limonene attracts many researchers into the field of waste tyre valorisation (Pakdel *et al.*, 2001). Limonene has many applications such as the formulation of industrial solvents and as a feedstock for the production of fragrances, resins and adhesives. Limonene is also used as a dispersing agent for pigments (Cunliffe and Williams, 1998).

The presence of hetero-aromatic compounds (Sulphur-, Nitrogen- and Oxygen containing) in TDO originates from vulcanising agents/accelerators that are added during tyre manufacturing (Trongyong and Jitkarnka, 2015). During pyrolysis, accelerators in tyres such as N,N-di-isopropyl-2-benzothiazole-sulfenamide, 2-(4-morpholinylthio)-benzothiazole, N,N-Carprolactamdisulphide and 2-mercaptobenzothiazole go through thermal degradation to produce the different hetero-aromatic compounds found in TDO (Quek and Balasubramanian, 2013).

TDO containing high concentrations of sulphur cannot be used directly as a fuel because of SO_x emissions (Trongyong and Jitkarnka, 2015).

PAHs are present in TDO as a result of secondary reactions at elevated temperatures (Cunliffe and Williams, 1998). A summary of the TDO chemical composition and the respective quantities of each species is given in Table 2.1.

Table 2.1: A summary of the TDO chemical composition (adapted from Banar *et al.*, 2012).

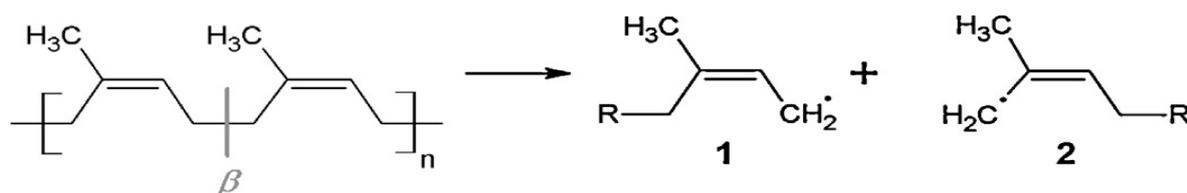
Species	Wt.%
Nonaromatic C5-C10	46.97
C5	6.82
C6	1.23
C7	1.03
C8	2.20
C9	0.76
C10	34.93
L-limonene	1.27

Table 2.1: A summary of the TDO chemical composition (adapted from Banar *et al.*, 2012) (*Cont.*)

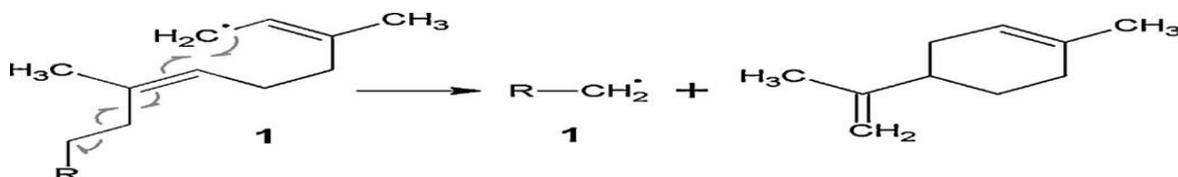
Species	Wt. %
D-limonene	25.53
Single ring aromatics	20.17
Benzene	0.21
Toluene	0.78
Xylenes	1.23
Ethylbenzene	0.52
Styrene	2.17
Benzene derivatives ≤C10	15.27 7.15
Polycyclic aromatic hydrocarbon	1.15
Naphthalene	0.24
Methylnaphthalenes	0.08
Trimethylnaphthalenes	0.14
Benzene derivatives	0.60
Phenanthrene	Below detection limit
Biphenyl	0.03
Nonaromatic C10+	12.45
S compounds	1.39
N compounds	1.33
O compounds	6.06

2.3.1 Formation of limonene

In nature, limonene exists as *dl*-limonene (dipentene) and *d*- and *l*-limonene. Limonene is obtained naturally from citrus oils. The natural production of limonene is low relative to its demand. In TDO, the dipentene racemic mixture form is present in high concentrations (Cunliffe and Williams, 1998). Limonene has been identified as a major constituent in TDO by several researchers (Kyari *et al.*, 2005; Murillo *et al.*, 2006; Stanciulescu and Ikura, 2006; Wei *et al.*, 2016). Scheme 2a is a representation of a reaction that produces limonene in TDO. The first step is the degradation of NR or *cis*-1,4-polyisoprene formed by scission of the β bonds with respect to the double bonds of the polymer chain to form isoprene radicals (Danon *et al.*, 2015). The final step is the intramolecular cyclization of the radicals to form dipentene.



Step 1: Thermal degradation of polyisoprene



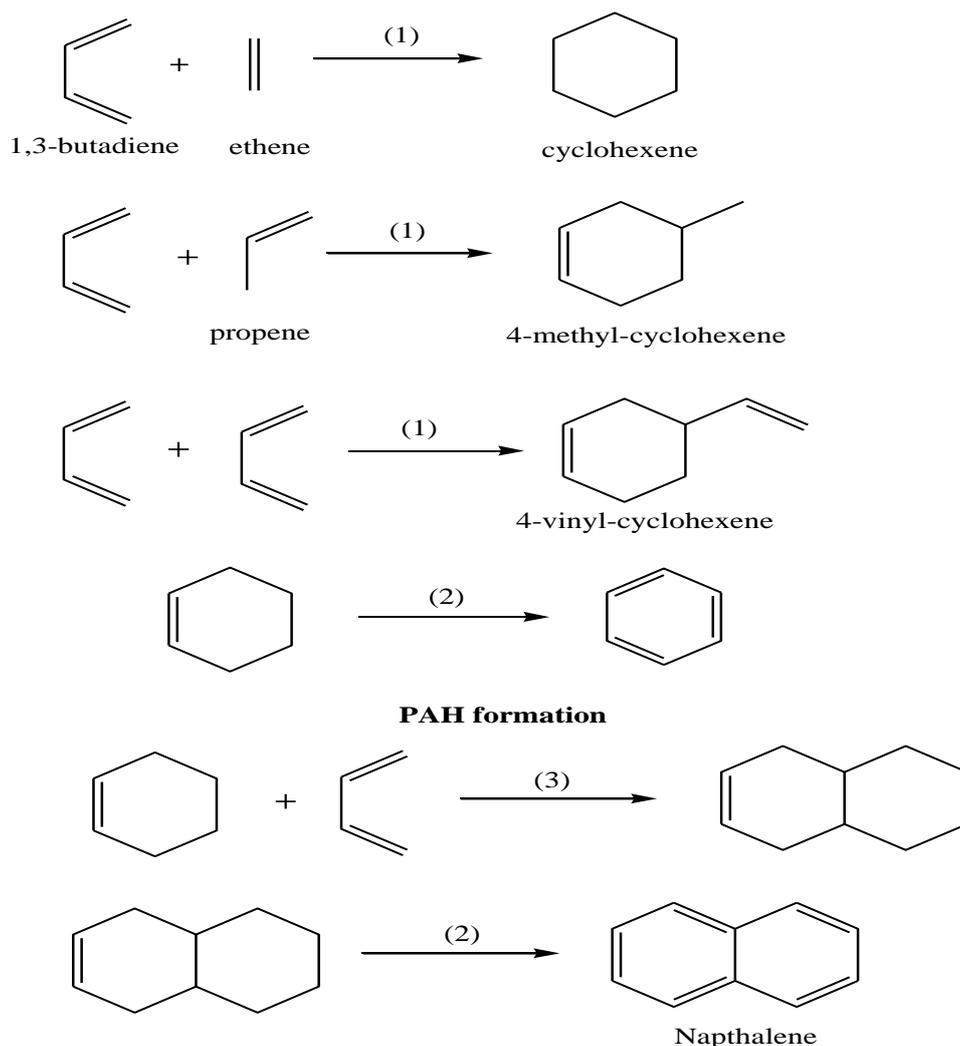
Step 2: Intramolecular cyclization to form dipentene

Scheme 2a: Pathway for the formation of limonene during pyrolysis of waste tyre (Adapted from Danon *et al.*, 2015).

At temperatures above 500 °C, limonene decomposes to a wide range of aromatic compounds such as trimethylbenzene, cymene, indane and BTX (Pakdel *et al.*, 2001; Williams, 2013). Trimethylbenzene, cymene and indane have a similar boiling point as limonene (≈ 176 °C) leading to the difficulties of limonene extraction by ordinary distillation. Limonene is the only non-aromatic compound in the azeotrope mixture with a molecular weight of 136 g/mol. Such properties offer great opportunities of discovering new methods of isolating limonene.

2.3.2 Formation of aromatic compounds and PAHs

Pyrolysis of waste tyre leads to the formation of ethene, propene and 1,3-butadiene which react as in Scheme 2b to form cyclic alkenes that further dehydrogenate to produce aromatic compounds such as BTX. Subsequent associative reactions of single aromatic compounds lead to the formation of PAHs (Cunliffe and Williams, 1998). TDO contains a wide range of PAHs such as alkylated naphthalenes, fluorenes, and phenanthrenes (Williams, 2013; Williams and Taylor, 1993; Cunliffe and Williams, 1998). The concentration of PAHs has been reported to increase with increasing pyrolysis temperature (Laresgoitti *et al.*, 2004). A Diels-Alder reaction mechanism has been suggested by various authors to be responsible for the formation of PAHs at higher pyrolysis temperatures (Cypres and Bettens, 1989; Williams and Taylor, 1993).



Scheme 2b: Formation of cyclic alkenes, aromatics, and PAHs during pyrolysis of waste tyre (Adapted from Williams and Taylor, 1993). Step (1), cyclisation; Step (2), Aromatisation; Step (3), Diels-Alder reaction.

2.3.3 Formation of hetero-aromatic compounds.

During pyrolysis, the C-S and N-S bonds present in accelerators added for vulcanizing rubber materials breakdown to form benzothiazole and caprolactum (Susa and Haydary, 2013; Lopez *et al.*, 2011). Benzothiazole is the most reported sulphur-containing species in TDO (Susa and Haydary, 2013). Similarly, cleavage of oxygen containing accelerators leads to the formation of oxygenated compounds in TDO. Benzothiazole can be isolated from TDO as a toxic species with an effort of reducing the sulphur content so as to enhance the application of TDO as an alternative fuel. Benzothiazole is also considered as a valuable species by many researchers (Yadav and Senthicumar, 2011) because of its applications in the tyre manufacturing industry as an accelerator and the medical industry. Additional hetero-aromatic compounds that have been identified in TDO include aniline,

cyclohexanone, cyclopentanone, thiophene, quinoline, and many others (Banar *et al.*, 2012; Unapumnuk *et al.*, 2008).

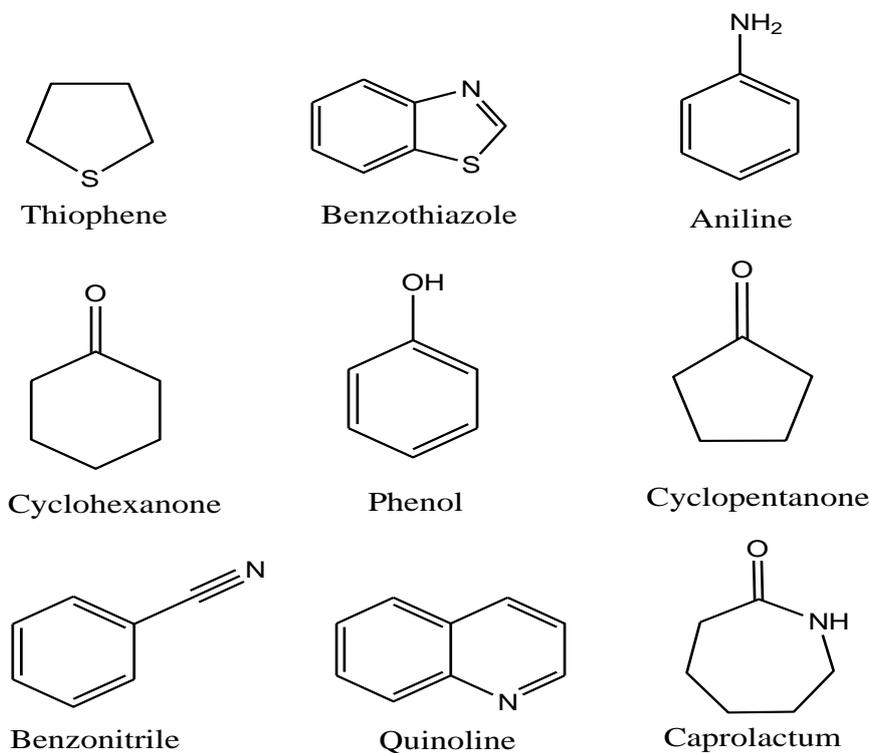


Figure 2.1: Examples of hetero-aromatic compounds reported to be present in TDO

2.4 Convectonal TDO purification methods

Distillation is the most used technique for TDO purification. Distillation separates components of a mixture according to their boiling points. When extracting limonene (176°C) from TDO, distillation only isolates the azeotrope mixture that consists of limonene, trimethylbenzene, indane and cymene. New distillation methods have emerged whereby an entrainer is added to the azeotrope mixture to alter the boiling points of the components. By this way, limonene can then be isolated in high concentrations through distillation.

Different techniques such as catalytic desulphurization, extractive desulphurization and oxidative desulphurization have been reported for desulphurizing oils. Catalytic desulphurization is the most common technique for reducing the amount of sulphur in TDO. This section provides the current state of art review for TDO purification, examples are also given for limonene recovery and sulphur reduction from TDO.

2.4.1 Distillation

According to several researchers (Laresgoitti *et al.*, 2004; Benallal *et al.*, 1995; Roy *et al.*, 1990), when TDO is processed by distillation, about 20% of the oil distillate under 170°C, this fraction is

called the light fraction and comprises of compounds such as BTX. Between 160 and 200°C, about 10% of the oil distillate to a fraction comprising mainly of heavy and long aliphatic compounds. It was also reported (Roy, 1993) that fractionating TDO by distillation at a temperature below 204°C produces a fraction containing several valuable chemicals. Particularly interesting chemicals identified in the fraction include benzene (80.1°C), Toluene (110.6°C), o-Xylene (144.4°C), m-Xylene (139.1°C), p-Xylene (138.3°C) and *dl*-limonene (176°C). Limonene was the major species in the fraction with a concentration of about 17 wt%.

In literature (Pakdel *et al.*, 2001; Stanciulescu and Ikura, 2006), it is reported that limonene isolation by distillation only result in a limonene enriched fraction which is a result of the decomposition of limonene during pyrolysis to yield compounds that have a similar boiling point as limonene. Upon investigating the separation of limonene from TDO, Stanciulescu and Ikura (2006) performed two distillation processes. The first was performed at a boiling point of 190°C and atmospheric pressure. The condensed fraction was enriched with limonene. Other components detected in the condensed fraction (boiling point less than 190°C) include benzene (3 wt%), toluene (11 wt%), styrene (8 wt%), m-xylene (23.8 wt%) and terpenes (26.6 wt %). Limonene was the most concentrated of all terpenes with an overall concentration of 63 wt%. Hetero-aromatic compounds (sulphur, nitrogen and oxygen-containing), cyclic and acyclic compounds were also detected. Sulphur content in crude TDO was 1.2 wt%, which is higher than 0.43 wt% in the condensed limonene enriched fraction. The sulphur content decreased because most of the sulphur containing components is in the heavy oil fraction. The second distillation process increased the limonene concentration to approximately 32-37 wt%.

Further efforts were made by Stanciulescu and Ikura (2006) to increase the limonene concentration. Efforts were made by introducing methanol and isopropanol in the limonene enriched fraction. The idea was to convert limonene via esterification (alkoxylation) to a more polar compound with a boiling point outside the limonene boiling range. Limonene ether (methyl ether) was formed with a boiling point of 198°C. Methyl ether was separated from the fraction through ordinary distillation. Aromatic compounds were still detected in the distillation product because of the poor selectivity (71.6 %) of the esterification reaction. Additional costs from such methods include re-distillation, alkoxylation reaction of methanol and limonene via a specific catalyst, distillation to separate limonene ether and cleavage to produce limonene from limonene ether. Other researchers (Danon *et al.*, 2015) still consider limonene separation from TDO a challenge that needs new affordable methods.

Pakdel *et al.* (2001) reported similar results as Stanciulescu and Ikura (2006). Most importantly Pakdel *et al.* (2001) also detected compounds with very similar boiling points after distillation of TDO at 195°C. Compounds detected with a boiling point similar to limonene were 1,2,3-trimethylbenzene, m-cymene and indane.

Purification of TDO through distillation for fuel use is the most commonly practiced around the world. Today TDO is being purified through distillation for fuel use in China (Beston® Engineering). Literature (Lopez *et al.*, 2011; ; Murugan *et al.*, 2008) shows that distilled TDO has similar properties with diesel and gasoline. The carbon and hydrogen content of distilled TDO is 85 wt% and 11 wt% respectively. Refined petroleum also has similar contents of carbon and hydrogen. The only challenge of using TDO as a fuel lies in its high sulphur content. Scientists today are driven to finding new ideas of purifying TDO because of two reasons. Firstly distillation is expensive due to its high energy demands. Secondly simple distillation fails to purify limonene from TDO.

2.4.2 Desulphurization

TDO has the potential of being applied as an alternative fuel for diesel engines. The fuel properties of TDO have been previously studied by researchers (Lopez *et al.*, 2011; Frigo *et al.*, 2013). The calorific value, flash point, density, viscosity and ultimate analyses were found to be similar to those of commercial fuels. The high sulphur content in TDO is an obstacle to utilization of waste tyres as an alternative fuel. Several researchers (Susa and Haydary, 2013; Trongyong and Jitkarnka, 2015; Olazar *et al.*, 2008) reported that TDO has a sulphur concentration ranging from 1.0 to 1.4 wt%. According to the South African National Standards (SANS 342), all commercial fuels must have a sulphur content of less than 500 ppm.

Desulphurization studies are usually performed through catalytic desulphurization, distillation and by manipulation of pyrolysis parameters. The high boiling fraction is the most concentrated with sulphur species, for example, benzothiazole (228°C). It is possible through distillation to obtain a petroleum fraction with low sulphur content by simply fractionating TDO into a low boiling and high boiling fraction (Link and Zandhuis, 2006). Pilusa (2017) studied the physical and chemical modifications of TDO by initially fractionating (gas-phase fractional distillation) TDO to recover the light to medium fraction. The obtained light fraction was then oxidised with iron oxide while capturing sulphur compounds in a gas phase. Oxidation with iron oxide reduced the low boiling sulphur compounds such as mercaptans. The levels of sulphur were still higher than recommended by SANS 342 for commercial fuels (< 500 ppm). Ca(OH)₂ and H₂SO₄ were later used to chemically reduce the TDO sulphur content. The overall sulphur reduction was 90.3% and still not efficient.

Upon investigating desulphurisation of TDO by a catalyst during pyrolysis, researchers (Trongyong and Jitkarnka, 2015) reported that Al-MCM-48 (Aluminosilicate Mobil composition of matter number 48) catalyst reduce sulphur in TDO by 5%. Al-MCM-48 showed poor selectivity as it also reduced the concentration of PAHs through promotion of ring opening reactions. Other catalysts, mainly zeolites, have also been reported to reduce sulphur content with poor selectivity in TDO (Unapumnuk *et al.*, 2008).

Some pyrolysis parameters have been reported to have an effect on the amount of sulphur in TDO. For example, as the pyrolysis temperature increases from 350 to 400°C, the amount of sulphur in TDO decreases (Unapumnuk *et al.*, 2008). Pyrolysis heating rate does not promote any desulphurization. Catalytic desulphurization and desulphurization by pyrolysis parameters have a common disadvantage of affecting the composition of other TDO components.

Pakdel *et al.* (2001) suggested that recovery of high purity valuable compounds from TDO will require two consecutive distillation processes followed by an extra purification step. A technique referred to as membrane pervaporation is commonly used nowadays for the separation of azeotropes. Pervaporation utilises composite membranes and a low pressure on the permeate side to evaporate the permeates (Seader *et al.*, 1998). Membranes have an advantage of separating components independent of their vapour-liquid equilibria. This study aims to utilise membranes for purification of TDO. The reduction of benzothiazole and recovery of limonene from TDO are the main priorities.

2.5 Organic solvent nanofiltration (OSN)

2.5.1 Introduction

As defined by Mulder (1996), “A membrane can be thick or thin, its structure can be homogeneous or heterogeneous, and transport can be active or passive and can be driven by means of pressure, concentration or a temperature difference. Membranes can also be natural or synthetic and can be charged or neutral”.

A membrane acts as a semi-permeable boundary that regulates the transportation of substances in a solution. As illustrated in Figure 2.2, the solution allowed to separate on the membrane’s surface is called the “feed”, whereas the solution that passes through the membrane is called the “permeate”. The solution that remains on the surface of the membrane after separation is referred to as the “retentate”. Membrane separations are induced by a driving force that is applied across the feed side of the membrane. The driving force can either be by a pressure gradient, concentration gradient, electric voltage gradient or temperature gradient (Beier, 2015; Padaki *et al.*, 2015). A membrane is more permeable to certain components of the feed solution than others because of differences in physical properties between the membrane and components of the feed solution (Mulder, 1996; Beier, 2015).

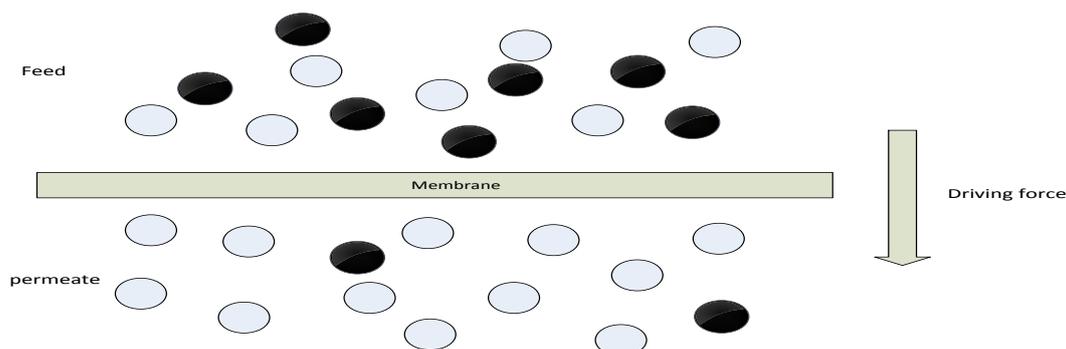


Figure 2.2: Illustration of a basic membrane separation process.

Membrane processes compete directly with many traditional separation techniques. When compared to other separation techniques, membrane processes are energy efficient, simple to use and often produce high quality separations. The advantages and disadvantages of membrane processes are summarised in Table 2.2. In some applications, membrane processes are costly but provide better product quality (Strathmann *et al.*, 2011)

Table 2.2: A summary of advantages and disadvantages of membrane processes

Advantages	Disadvantages
Energy efficient	Long-term reliability not proven
Simple operation	Distraction of active layer by high temperature and <i>pH</i>
Easy installation	Concentration polarization and fouling
Easy scale-up	High sensitivity to organic chemicals and operational errors

The poor long term stability of membranes upon contamination with organic solvents is a major concern that leads to industrial companies hesitating to adopt membrane processes as their traditional separating tool.

Fouling is the process by which the membrane's performance subsides due to the distraction of the membrane's active layer (Beier, 2015; Vandezande *et al.*, 2008). Concentration polarization is a phenomenon whereby macromolecules form a layer on the surface of a membrane creating resistance to permeating components of the feed solution (Jaffrin, 2015). Concentration polarization may either be due to accumulation of solids on the surface of the membrane or growth of biological films on the membrane's surface and pores. Concentration polarization results in pore blockage and the subsequent inhibition of solute permeation across the membrane.

Membrane processes are classified according to their ability to separate specific sizes of molecules. Membrane classification includes microfiltration (MF), ultrafiltration (UF), Nanofiltration (NF) and

reverse osmosis (RO). It can be seen from Figure 2.3 that membrane processes have the ability to separate all kinds of particles, from ions to relatively large particles. Table 2.3 summarises the classification of membrane processes according to their permeance and operating pressures (Beier, 2015; Padaki *et al.*, 2015).

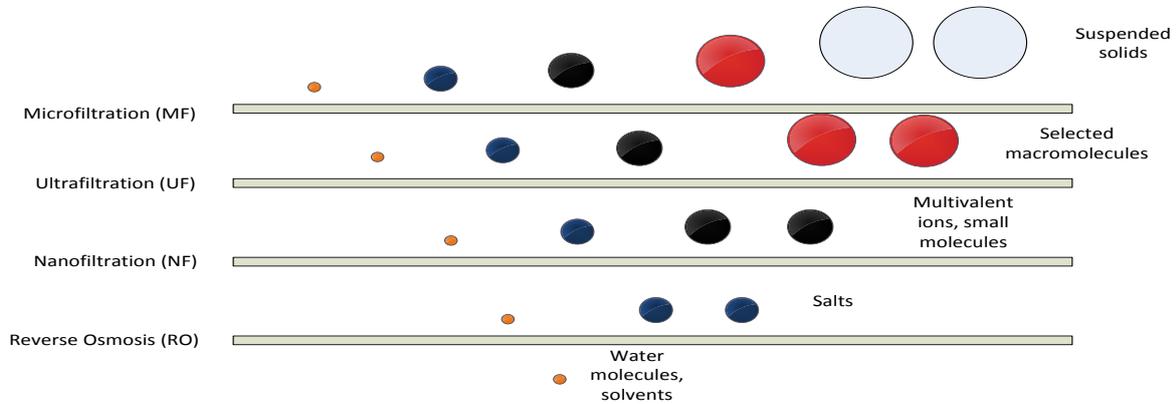


Figure 2.3: Membrane classification according to particles separated.

Table 2.3: Membrane classification according to operating pressure and permeance (Beier, 2015; Mulder, 1996)

Membrane process	Operating pressure (bar)	Permeance ($\times 10^{-3} \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$)
Microfiltration	0.1-3	>50
Ultrafiltration	2-10	10-50
Nanofiltration	5-30	1-15
Reverse osmosis	10-100	<1

NF is a pressure-driven membrane process that is capable of separating particles in the lower size (0.1-20nm) (Sereewatthanawat *et al.*, 2008). NF is intermediate between RO and UF offering greater rejections than UF and permeation rates higher than RO. Applications of NF are in waste water treatment, extraction of small molecules and fractionation (Jaffrin, 2015; Sun *et al.*, 2015; Gherasim *et al.*, 2015).

There are two fundamental models of operating pressure driven membrane processes such as NF. These are 1) cross-flow and 2) dead-end as illustrated in Figure 2.4.

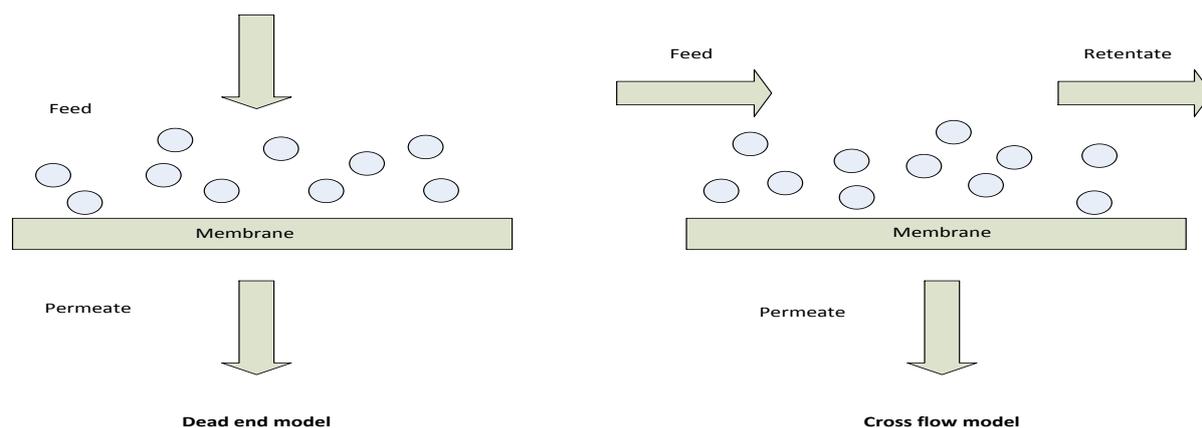


Figure 2.4: Comparison between dead-end and cross-flow model.

For the dead-end model, the feed is forced through the membrane by a pressure applied perpendicularly to the membrane surface, whereas in cross-flow the feed flows parallel to the membrane surface (Vandezande *et al.*, 2008). Dead-end model is advantageous when it comes to operating costs, ease of construction/installation and use. The major drawback of dead-end model is that it is more vulnerable to concentration polarization due to build-up of particles on the surface of the membrane (Mason and Lonsdale, 1990). Better filtration performances are often recorded with cross-flow than dead-end models. Cross-flow models minimise the chances of concentration polarization as the feed continuously washes the membrane surface. Cross-flow models are characterised by complex operating procedures (Beier, 2015).

Membranes are fabricated by either organic or inorganic matter. Organic membranes are constructed either by using synthetic or natural polymers and are more favoured due to their greater flux and low cost. Inorganic membranes are ceramic and considered to be best with chemical and thermal stability. Ceramic membranes are more expensive, easy to break and up-scaling is difficult. The performance of polymeric membranes is greatly affected by temperature, solvent type and pressure (Szekely *et al.*, 2014; Volkov *et al.*, 2008). The active layer of polymeric membranes is often fabricated with polymeric materials such as polyimide (PI), polydimethylsiloxane (PDMS) or polyamide (PA) because of their strong tolerance to chemicals and temperature (Soltane *et al.*, 2016; Sereewatthanawat *et al.*, 2008). For OSN, membranes must possess greater chemical and mechanical resistance, exhibit high solvent fluxes and high retention of specific target compounds. The active layer of the polymeric membrane is often rearranged by organic media through the process called swelling. Swelling increases transport through the membrane but adversely affect selectivity of the separation (Volkov *et al.*, 2008).

2.5.2 Principles of OSN

OSN utilises solvent resistant polymeric membranes to selectively retain nanoscale particles (200-1000 g/mol) while allowing smaller particles to pass through (Lutze and Gorak, 2013; Sereewatthanawat *et al.*, 2008). Solvent resistant nanofiltration (SRNF) is another name that is used to describe OSN in literature (Vandezande *et al.*, 2008). Membranes designed for other applications such as water treatment dissolve or swell upon contact with organic solvents (Szekely *et al.*, 2014; White and Nitsch, 2002). In addition to advantages given for membrane processes, OSN brings forth an extra advantage of operating in organic media.

Molecular weight cut-off (MWCO) is an important parameter of OSN membranes that refers to the molecular weight at which the membrane achieves 90% rejection of a specific solute (Janssen *et al.*, 2011). MWCO is considered as the most important parameter to look at when selecting a membrane for a specific separation process. Other properties that should be considered when selecting a membrane are membrane properties (pore size, polarity, surface tension, etc.), solute properties (solubility, polarity, size, Geometry, viscosity, etc.), solvent properties (same as solute properties) (Lutze and Gorak, 2013).

The performance of a membrane process is assessed in terms of flux (J) and percentage rejection (R) (Saravanan *et al.*, 2006). Flux is defined as the amount of liquid that passes through the membrane per unit time and surface area and can be estimated using Equation 2.1.

$$J = \frac{V}{A \times t} \quad (2.1)$$

Where

J is the flux (L.m⁻².h⁻¹)

V is the volume of collected permeate (L)

A is the active surface area (m²)

t is the time (h)

Rejection is defined as the ability of a membrane to reject a solute. Equation 2.2 is used to calculate the membrane's rejection.

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (2.2)$$

Where

C_p Is the concentration of the solute in the permeate stream (mg/L)

C_f Is the concentration of the solute in the feed stream (mg/L)

The establishment of maximum permeate flow and solute rejection with minimal capital and operating cost is the principal task in optimal design of membrane processes (Makhan *et al.*, 2000). Permeate fluxes and membrane lifetimes are primarily affected by concentration polarization and fouling at the membrane surface (Khulbe *et al.*, 2000). Concentration polarization is considered as a reversible phenomenon whereas fouling is complicated and considered as irreversible (Sablani *et al.*, 2001). The main factors leading to the irreversible loss of membrane permeability are adsorption of feed components, deposition of solids on the membrane surface and compaction of the membrane structure. The primary reason for flux decline during the initial stages of a membrane separation process is concentration polarization at the membrane surface (Afonso *et al.*, 2001; Sablani *et al.*, 2001).

Two models of describing the concentration polarization phenomenon are the gel polarization model and the osmotic pressure model (Sablani *et al.*, 2001; Van den berg and Smolders, 1990).

Gel polarization model

The gel polarization was the first model proposed for explaining the effects of concentration polarization in pressure-driven membrane processes (Porter, 1972). The basic assumption of this model describes that beyond a certain value of applied pressure, the membrane permeation rate is limited by the presence of a gel layer deposited on the membrane surface which increases effective membrane thickness and so reduces its hydraulic permeability. Once the gel layer is formed, increasing the applied pressure only increases the thickness of the gel layer but not the flux (Van den berg and Smolders, 1990).

Osmotic pressure model

The osmotic pressure model regards the limiting flux as a consequence of the increased osmotic pressure produced by the high concentration of the rejected solute near the membrane surface (Sablani *et al.*, 2001). Ebbing and Gammon (2009) defines osmotic pressure as a colligative property of a solution equal to the pressure that, when applied to the solution, just stops osmosis. Van den berg and Smolders (1990) explained that a macromolecular solution generally has a very small osmotic pressure. However, during the filtration of a macromolecular solution, a large concentration build-up can be realized. The osmotic pressure of the concentration build-up can increase to high values and result in concentration polarization. The use of a stirrer in the membrane cell can minimise concentration polarization (Porter, 1972).

2.5.3 Review of oil processing by membranes

To the author's knowledge, there is currently no publication in relevant literature addressing the purification of TDO using membrane technology. However, several researchers (Darvishmanesh *et al.*, 2011; Blistad and Espedal, 1996; Torres *et al.*, 2016) studied the purification of various oil-systems using membrane technology. In this section, a literature review is presented concerning the separation of components of various oils by membranes. The aim of this section is to present the state of the art review of studies conducted on oil-systems using membrane technology. Table 2.4 is a summary of OSN applications in the oil industry. The different polymer materials used for the membranes are important.

Table 2.4: Summary of OSN applications in the oil industry (Summarised from Priske *et al.* 2016)

Application	Membrane material
Fractionation of hydrocarbon oils	P/carbonate
Vegetable oil deacidification	PA
Aromatics from heavy oil	P/propylene
Oils from organic solvents	PI
Vegetable oil refining	PI/PDMS/PVA/PAN
Recovery of metals from heavy oil	PVDF

Major applications of OSN are found in the oil- and petrochemical industry. The world's largest commercial implemented OSN process, Exxon Mobile's and W.R Graces' Max-Dewax®, is provided by the oil- and petrochemical industry. Major applications under the oil- and petrochemical industry include degumming of vegetable oil, dewaxing of lube oil, biodiesel production and conditioning of liquid hydrocarbons (Priske *et al.*, 2016). Dewaxing and degumming are processes aimed for the removal of fat-soluble impurities in oil. Biodiesel is not the only product formed by the transesterification reaction between a monohydric alcohol and triglycerides, glycerol and other by-products are also formed and have to be removed to ensure quality biodiesel production.

One of the work's that led to the installation of a commercial membrane plant trademarked Max-Dewax® was performed under solvent recovery from lube oil filtrates by a polyimide membrane (White and Nitsch, 2000). The work expanded the conventional solvent lube-oil dewaxing process by combining it with a membrane system that is designed to recover the solvent (MEK and toluene) in high purities. Performance data showed good rejection of lube oil (98%) and significant solvent flux (16.1 L.m⁻².h⁻¹). After 60 days of continuous operation, the polyimide membrane demonstrated remarkable solvent recoveries from lube oil filtrates at a purity of higher than 99% with a steady flux. This work demonstrated the excellent chemical resistance and performance of the polyimide

membrane. In 2002, White and Nitsch also reported that polyimide membranes have excellent chemical resistance, viable flux and rejection characteristics for the separation of light hydrocarbon solvents from lube oil. The study also mentioned that membrane materials designed for reverse osmosis dissolve upon contact with methyl acetate, ketone and toluene.

The extraction of vegetable oil is commonly practiced by the use of toxic solvents and high energy consuming processes such as distillation and evaporation to recover the solvent. Darvishmanesh *et al.* (2011) presented a membrane based extraction method that utilises commercial NF membranes to recover the solvent from the oil/solvent mixture. The membranes used were Desal-DK-polyamide NF from GE-osmonics®, STARMEM™ 122 (PI) from Membrane Extraction Technology®, and SOLSEP NF030306 silicone base polymer from SOLSEP®. The Desal-DK polyamide membrane showed visible defects on its surface after exposure to acetone and as a result its filtration performance was poor. The ST™ 122 and SOLSEP NF030306 showed good filtration performances with acetone, ethanol and isopropanol. ST™ 122 membrane achieved an acetone flux and oil rejection of $16.8 \text{ L.m}^{-2}.\text{h}^{-1}$ and 70% respectively while SOLSEP membrane managed to achieve an acetone flux of $4.8 \text{ L.m}^{-2}.\text{h}^{-1}$ with 78% oil rejection.

Crude vegetable oil contain impurities such as phospholipids and free fatty acids that precipitate during storage of oil and develop an unpleasant odour which renders the oil unsafe to use. A study (Desai *et al.*, 2002) on degumming of vegetable oil by membrane technology demonstrated that membrane based separations can simultaneously remove phospholipids and colour at room temperature from vegetable oils. The study was conducted using UF and NF membranes, MWCO was 2 50 000 Da and 1000 Da respectively. UF membranes showed higher oil flux ($105 \text{ L.m}^{-2}.\text{h}^{-1}$) than NF membranes ($15 \text{ L.m}^{-2}.\text{h}^{-1}$) whereas the rejection of phospholipids was higher for NF (96%) than for UF (39%). The observed results are probably due to the fact that UF membranes have larger pores than NF membranes. Larger pores increases oil permeability while decreasing retention of oil components. The study also indicated that oil flux highly depends on the pressure applied. Other researchers (Manjula and Subramanian, 2006; Saravanan *et al.*, 2005) prefer using hydrophobic nonporous membranes for processing vegetable oil because they give a near total rejection of phospholipids with oil flux being low. When processing oils or any solution on a membrane, it is very important to use the right membrane that will retain high amounts of specific target compounds with an average to high oil flux.

The production of biodiesel from vegetable oil and a short chain alcohol (methanol) produces by-products such as glycerol, triglycerides, monoglycerides, diglycerides, solvents and water (Ma and Hanna, 1999). Researchers (Torres *et al.*, 2016) came up with a new method of purifying biodiesel, which involves using UF membranes that are resistant to solvent and alkalis. The UF membranes tested were made up of PVDF and PSF materials and had MWCO's of 7 and 5 kDa respectively. The

PVDF membrane reached a glycerol (92.09 g/mol) rejection of up to 67.3% and a permeate flux of 9.5 L/(cm²h). More interesting, stability tests showed that the PVDF membrane is more stable to solvents. The PSF membrane showed high chemical stability and low fouling by demonstrating a flux recovery after more than 45 cycles of permeation. Solvent resistant membranes are more favoured by researchers because they preserve their separation characteristics after a number of operating cycles. New methods such as these will make membrane technology more competitive with traditional oil purification methods.

Just like TDO, oily wastewater has a complex hydrocarbon mixture. Reviews (Padaki *et al.*, 2015; Manirasu *et al.*, 2016) on oil-water separation by membrane technology highlighted the different compounds found in oily wastewater to be aliphatic, aromatic, hetero-aromatics (nitrogen-, sulphur- and oxygen-containing compounds) and asphaltenes. The processing of oily wastewater by a membrane can be related to that of TDO due to their similar chemical composition. Padaki *et al.* (2015) used and recommended UF membrane processes as the most effective for treating oily wastewater. UF membranes demonstrated approximately 96% rejection of total hydrocarbon concentration and about 56% rejection of BTX. From the reported results, it can be safe to say that NF membranes will increase the rejection of BTX and other compounds that are in the same molecular weight range. As a result of the complex hydrocarbon mixture of oily wastewater, concentration polarization has been identified as the main drawback of processing oily wastewater by a membrane (Stroller *et al.*, 2016). It is generally agreed that using hydrophilic membranes decreases the adhesion of oil on the membrane surface which then results in less concentration polarization on the membrane surface (Mansourizadch *et al.*, 2014). A summary of previous publications including the year of publication is presented on Table 2.5.

Table 2.5: Summary of previous publications on processing of oils by membranes

Year	Field	Solvent	Membrane (Classification, polymer type, etc.)	Result (Flux & oil rejection)	Reference
2000	Oil dewaxing	MEK/Toluene	UF (PI)	16 L.m ⁻² .h ⁻¹ , 98%	White and Nitsch (2000)
2002	Vegetable oil purification from phospholipids	Methanol	UF (PSU)	87 L.m ⁻² .h ⁻¹ , 39%	Desai <i>et al.</i> , (2002)
			UF (PSU)	51 L.m ⁻² .h ⁻¹ , 41%	
			UF (PES)	42 L.m ⁻² .h ⁻¹ , 95%	
			NF (Cellulose)	11 L.m ⁻² .h ⁻¹ , 94 %	
2011	Solvent purification from oil-solvent mixture	Ethanol	ST-122	17.4 kg.m ⁻² .h ⁻¹ , 96%	Darvishmanesh <i>et al.</i> , (2011)
			Solsep NF03038	4.89 kg.m ⁻² .h ⁻¹ , 78%	
		Isopropanol	ST-122	4.48 kg.m ⁻² .h ⁻¹ , 79%	
		Acetone	ST-122	56.6 kg.m ⁻² .h ⁻¹ , 70%	
			Solsep NF03038	16.6 kg.m ⁻² .h ⁻¹ , 78%	
			NF30 and GK DK	Not stable	

Table 2.5: Summary of previous publications on processing of oils by membranes (*Cont.*)

Year	Field	Solvent	Membrane (Classification, polymer type, etc.)	Result (Flux & oil rejection)	Reference
2011	Solvent purification from oil-solvent mixture	Cyclohexane	Solsep NF03038	0.54 kg.m ⁻² .h ⁻¹ , 64%	Darvishmanesh <i>et al.</i> , (2011)
		Hexane	Solsep NF03038	0.55 kg.m ⁻² .h ⁻¹ , 38%	
1996	Oil-water separation	No solvent	NF membrane (100,000 Da)	96% THC 54% BTX, 140 L.m ⁻² .h ⁻¹ 95% Metals	Bilstad and Espedal (1996)
2016	Biodiesel purification from glycerol, triglycerides, monoglycerides and diglycerides.	Ethanol	PVDF-20-5 (UF) PSF-23-7 (UF)	63%, 9.5 L.m ⁻² .h ⁻¹	Torres <i>et al.</i> , (2016)

Concentration polarization is a common challenge that occurs when processing different oils by membranes. The viscous nature and high concentration of molecules in oils influences concentration polarization which guarantees poor membrane performance. High oil fluxes are often observed when ultrafiltration membranes are used to process the oil. Volume fluxes of 105, 15 and 9.5 L.m⁻².h⁻¹ are reported in literature for ultrafiltration membranes (Desai *et al.*, 2002; Torres *et al.*, 2016). Researchers (Darvishmanesh *et al.*, 2011; White and Nitsch, 2000) have also reported high oil rejections (> 70%) with nanofiltration membranes. Membranes demonstrating low oil fluxes or high oil rejections will result in poor separations of the oil constituents.

A recent publication (Werth *et al.*, 2017) did simulation studies on the potential of OSN processes in oleochemical industries. Aspen custom modeller[®] (ACM) was used for modelling and optimization of OSN processes. Most fascinating about the findings of the study is the effect of concentration polarization on OSN processes. Previous publications (Silva *et al.*, 2010) also highlighted that it is important to consider concentration polarization when modelling flux and rejection for systems with high solute concentrations. The present study focuses on a highly concentrated system, TDO. To minimise concentration polarization, a magnetic stirrer bar is placed at about 3 mm above the membrane. The function of the stirrer bar is to prevent molecules from settling on the surface of the membrane. The modelling and optimization studies by Werth *et al.* (2017) also pointed out that OSN processes in oleochemical industries have the potential of reducing energy demands by more than 70%.

Purification of limonene from its counterparts (p-Cymene, trimethylbenzene and indane) is referred to as “separation on a molecular level”. This aspect is still a challenging issue with membranes.

Gilmer and Bowden (2016) focused on the very same challenge by attempting to separate various organic chemicals with OSN membranes. The organic chemicals weighed between 100 and 300 g/mol. Polyepoxy membranes of different MWCO's (195 – 500 g/mol) were used. Table 2.6 presents the relative flux of six different chemicals through OSN membranes of different MWCO. The flux of tri(p-tolyl) phosphine (304.37 g/mol) was set as the standard for each membrane, and the flux of each chemical was reported in relation to the flux of tri(p-tolyl) phosphine.

Table 2.6: Relative fluxes of molecules through a series of OSN membranes (Adapted from Gilmer and Bowden, 2016).

Molecules	MW (g/mol)	Membrane MWCO					
		500	400	350	283	237	195
p-nitrobenzaldehyde	151.12	10	20	167	250	100	90
Triethylamine	101.19	10	18	111	167	50	39
Tripropylamine	143.27	6	8	44	50	15	9
Tributylamine	185.36	3	3	27	25	7	3
Triphenylmethane	244.43	3	3	7	3	4	0
Tri(p-tolyl) phosphine	304.37	1	1	1	1	1	0

It can be seen from Table 2.6 that p-nitrobenzaldehyde and triethylamine permeated at a flux that is 10 times higher than that of tri(p-tolyl) phosphine through a membrane of 500 g/mol MWCO. Table 2.6 also shows that p-nitrobenzaldehyde (151.12 g/mol) and triethylamine (101.19 g/mol) had the same flux through a membrane of 500 g/mol MWCO. As the MWCO decreased from 500 to 283 g/mol, the separation of p-nitrobenzaldehyde and triethylamine increased. This is an indication that the use of high porous membranes is not applicable to low sized molecules. Large pores will not pose any restriction to permeating substances while small pores will restrict the heavy, long and branched molecules. The same trend is also visible with tributylamine (185.36 g/mol) and triphenylmethane (244.43 g/mol). The separation became better as the MWCO decreased.

2.6 Concluding remarks

Chapter 2 provided detailed information to show that TDO is concentrated with valuable chemicals such as limonene. Other valuable chemicals include aromatic compounds (BTX) and hetero-aromatic compounds. Recovery and purification of the valuable chemicals is a challenge that researchers face today.

Distillation is the most used and investigated technique for purifying TDO. Recovery of limonene through ordinary distillation is ineffective because TDO contains other components with the same boiling point as limonene. Stanciulescu and Ikura (2006) distilled TDO under 190°C and detected m-cymene, indane and 1,2,3-trimethylbenzene as chemicals sharing the same boiling point with limonene. Pakdel *et al.* (2001) suggested that recovery of limonene will require two consecutive distillation processes followed by a purification step. Apart from the high energy demands, limonene separation by distillation is complex and requires additives for better separations. Several researchers

(Danon *et al.*, 2015) still consider limonene isolation from TDO a challenge that needs alternatives. This study aims to implement a cost-efficient, reliable and non-complex way for purifying TDO.

Organic solvent nanofiltration is an advanced form of membrane technology offering separations in non-aqueous systems. OSN is energy efficient since it separates components without the need of changing the molecular phase. Membranes separate components on the basis of molecular weight, viscosity and solute-membrane interactions (polarity, solubility parameter, dipole moment and surface tension). This study aims to purify TDO through the use of OSN membranes.

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CHAPTER 3

Materials and Methods

3.1 Overview

All experimental procedures and materials used in this study are presented in this chapter. This chapter is divided into 6 sections. Section 3.2 presents details about the membranes, TDO and chemicals used in this study. Section 3.3 presents the analytical instrument used and procedures followed for TDO chemical composition analysis and quantification. In Section 3.4, the focus is shifted to the OSN equipment used and procedures followed for OSN experiments. Section 3.5 concludes this chapter by providing an experimental design via a flow chart to highlight all manipulated and constant variables of this study.

3.2 Materials

3.2.1 Membranes used

Commercially available OSN membranes are still rare, hindering the use and application of OSN. The Puramem® and the Duramem® series was purchased from Membrane Extraction Technology (MET). The STARMEM™ series was purchased from Evonik industries. Duramem®, Puramem® and STARMEM™ membranes were selected for this study due to their interesting characteristics shown in Table 3.1. To protect against contamination and drying out, OSN membranes are soaked in preservation oil during manufacturing and supplied in a dry form.

Table 3.1: Summary of OSN membranes supplied by MET and Evonik industries

	Puramem®280	STARMEM™-228	Duramem®200
MWCO	280	280	200
Membrane material	Modified Polyimide	Polyimide	Modified Polyimide
Membrane type	Hydrophobic	Hydrophobic	Hydrophobic
Solubility parameter ^[a]	27.0 MPa ^{0.5}	27.0 MPa ^{0.5}	27.0 MPa ^{0.5}
	Stable in:	Stable in:	Stable in:
	Toluene	Alcohols	Ethanol
	Heptane	Hexane	Acetone
	Hexane	Toluene	Methanol
	Methyletherketone	Dichloromethane	Tetrahydrofuran
	High boilers and more	Acetone	
		Methyletherketone	

[a] solubility parameter estimated based on Lenzing P84 (Soroko *et al.*, 2011; Vandezande *et al.*, 2008)

l-limonene (99 vol%), *d*-limonene (99 vol%), benzothiazole (96 vol%), 1,2,4-trimethylbenzene (98 vol%), *p*-cymene (99 vol%), *d*-limonene (97 vol%), Indane (98 vol%), 2-ethyltoluene (98 vol%), dichloromethane (DCM) (99.8 vol%) and toluene (99 vol%) were all purchased from Sigma Aldrich and used for calibrations. The internal standards, α -pinene (99.8 vol%), deuterated naphthalene (99 vol%) and deuterated toluene (99 vol%) were also purchased from sigma Aldrich. DCM was used as a solvent for preparing standards and for gas chromatography analysis. Pure toluene was also used for membrane pretreatment. High purity nitrogen gas was purchased from Afrox and used to provide pressure inside the membrane cell.

3.3 Instrument used and TDO characterisation

3.3.1 Gas chromatography (GC)

The Agilent 7820A gas chromatography (GC) coupled to a flame ionization detector was used to quantify the solutes in the feed, permeate and retentate sample solutions. A capillary column in the oven had dimensions 60 m \times 180 μ m \times 0.10 μ m. The temperature programming in the oven initially had a temperature of 40°C that was held for 5 minutes. The temperature was then ramped at a rate of 0.7 °C/min to 104 °C and then at 10°C/min to 280°C where it remained for 5 minutes. The total run time of this method was 119.03 minutes. Helium was the carrier gas with an inlet pressure of 348 kpa.

3.3.2 TDO sampling procedure

Crude TDO cannot be directly injected into the GC instrument because of several faults that might occur. Injection of crude TDO might result in contamination of the column with high boiling point or non-volatile molecules that are present in TDO. This project adopted the validated work done by Ngxangxa (2016) in developing a GC method for the analysis of tyre derived oils. As described by Ngxangxa (2016), the sampling method referred to as solvent dilution was used to prepare TDO samples for analysis.

DCM was used as the solvent for preparing a TDO sample to be analysed for chemical composition by gas chromatography. The dilution factor of 1:100 (0.1 mL TDO added to 9.9 mL of DCM) was applied.

3.3.3 Quantification of TDO components

TDO components were quantified using the internal standard (IS) method. The internal standard method requires construction of calibration curves whereby the relative peak areas (analyte peak area divided by IS peak area) of standard solutions are plotted against known concentrations of the analyte (Unice et al., 2012). The calibration curve works by interpolating the relative peak area of the compound of interest in the sample to the curve to determine its concentration. Examples of calibration curves are shown in Figure 3.2. This method accounts for inaccuracy that might occur from sample preparation steps. The IS must be a compound absent from the entire composition of the

sample and must also be chemically similar to the compound of interest. In this investigation, α -pinene was used as an IS for limonene quantification, naphthalene-d₈ was used as an IS for benzothiazole quantification and toluene-d₈ was used as an IS for aromatic compounds.

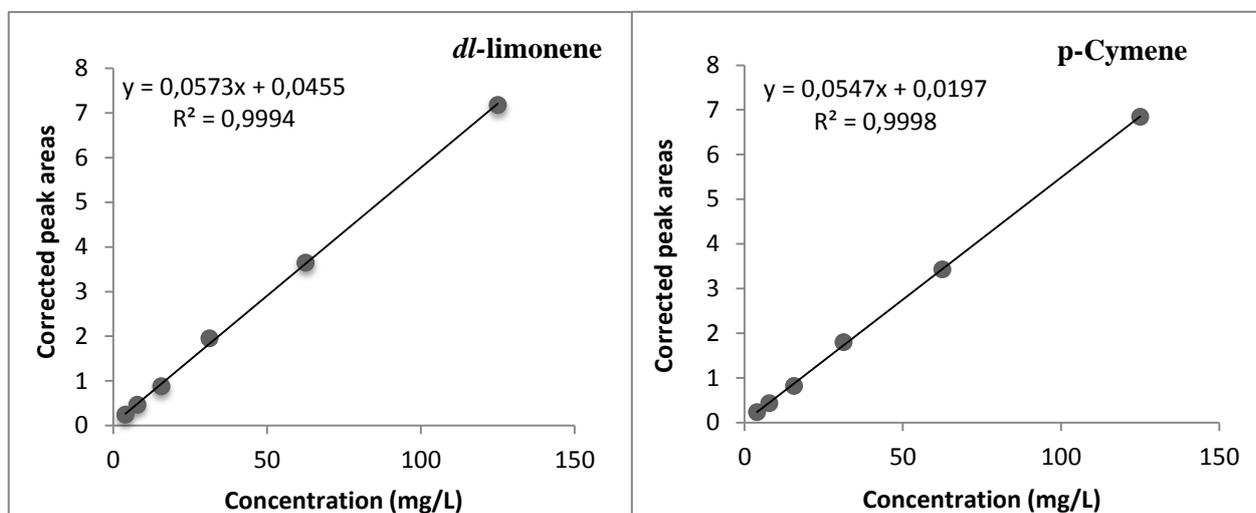


Figure 3.2: Example of calibration curves plotted for limonene and p-Cymene using α -pinene and toluene-d₈ respectively as internal standards.

The internal standards were added during TDO sampling by the solvent dilution method. Calibration curves were obtained by using specific concentration levels of standard solutions. The standard concentrations used were 3.91, 7.81, 15.6, 31.3, 62.5 and 125 mg/L. Each standard solution contained 20 mg/L of the IS.

3.4 OSN permeation experiments

3.4.1 Equipment used

A dead-end standard OSN set-up, as shown in Figure 3.3, was used to perform OSN permeation experiments (Van der gryp *et al.*, 2010; Xiao *et al.*, 2013; Xaba *et al.*, 2010; Peddie, 2017). The membrane pressure cell was made of stainless steel. Figure 3.3 shows a picture of the membrane pressure cell used for this investigation.

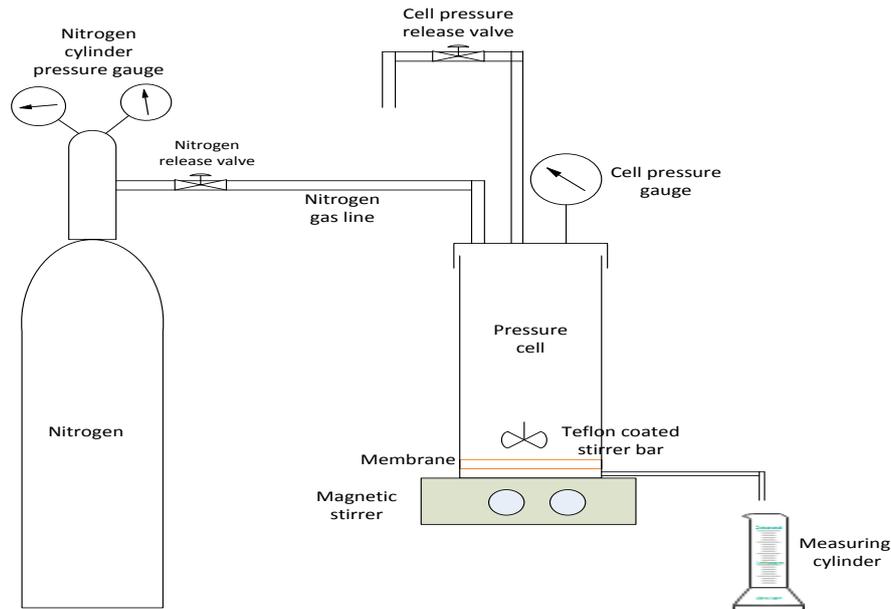


Figure 3.3: OSN experimental set-up used in this investigation



Figure 3.4: Stainless-steel membrane pressure cell

The maximum volume capacity of the pressure cell is 300 ml with an inner diameter of 46 mm. The membrane is located at the bottom of the cell and is supported by a stainless steel porous circular sintered plate. The membranes were provided as A4 sheets by the supplier and were cut to give a membrane active surface area of 16 cm² that fits perfectly on the plate that supports the membrane. The active surface area of the membrane is the area that is in direct contact with the feed. To minimise concentration polarization, a teflon-coated magnetic stirrer bar was fitted about 3 mm above the membrane surface. A stirrer speed of 500 rpm was used to create a homogenous mixture throughout all permeation experiments as a measure of minimising concentration polarization.

3.4.2 Experimental methodology

Before the membrane was subjected to characterisation, several procedures were followed so as to fully access the performance of the membrane. A typical separation experiment by a membrane under OSN consists of three steps: 1) membrane pretreatment, 2) membrane conditioning and steady-state characterisation, 3) flux and solute rejection characterisation. Toluene was chosen as a solvent for membrane pretreatment because of its low molecular weight, stability with OSN membranes and its reported presence in TDO. A detailed experimental procedure is given on Appendix A.

3.4.2.1 Membrane pretreatment

Membrane pretreatment is required for washing out or removing the preservation oil that comes with the membrane as a measure against contamination and drying out.

200 ml toluene was loaded in the cell and allowed to permeate through the membrane while the cell is being pressurized at 30 bar. After 150 ml of toluene has permeated through the membrane, the cell was depressurized and 150 ml of fresh toluene was loaded in the cell again. This sequence was repeated at 30 bar until the oil is completely removed from the membrane surface. Pretreatment was confirmed by attaining a steady-state toluene flux or observing no sign of colour on the permeate. Before initiating the next step, the cell was rinsed with 5 ml of TDO to avoid excess toluene from contaminating the next experiment.

3.4.2.2 Membrane conditioning and steady-state characterisation

Prior to characterisation, the membrane is required to adapt and attain a steady flux at a specific pressure. The aim for this is to minimise gradual changes during characterisation that might take place on the membrane surface. TDO was allowed to permeate through the membrane until the permeate flux is stable and constant. Membrane pretreatment was only done once for each membrane whereas membrane conditioning was done every time the pressure was changed.

Conditioning was done by allowing 250 ml TDO to permeate through the membrane at a specific pressure (10, 20, 30 and 40) until steady-state is achieved. After 150 ml has permeated, the membrane cell was depressurized and the permeate returned back into the cell as the feed to restart the process. Stopping and restarting was performed up until a constant flux was obtained. Flux was estimated (Equation 2.1) by measuring the time intervals, Δt , at which 20 ml TDO has permeated for a given active membrane surface area, A (Saravanan *et al.*, 2006).

$$J = \frac{V}{A \times \Delta t} \quad (2.1)$$

3.4.2.3 Characterisation of membrane performance

The feasibility of the membrane to purify TDO was evaluated by estimating its flux and rejection capability. Rejection estimation was achieved by quantifying both limonene and benzothiazole before and after TDO fractionation.

250 ml TDO was allowed to permeate through the membrane at a specific pressure. After fractionation, the permeate and retentate were analysed and quantified for limonene and benzothiazole. The quantities of limonene and benzothiazole before and after fractionation were used to estimate the rejection using Equation 2.2 (Saravanan *et al.*, 2006).

$$R = \left(1 - \frac{c_P}{c_f}\right) \times 100\% \quad (2.2)$$

3.5 Experimental design

The aim of this study was to investigate the possible feasibility of purifying TDO using OSN membranes. Different parameters were manipulated during filtration so as to fully assure the feasibility. As shown in Figure 3.5, this section presents an overview of the experimental design followed in this study.

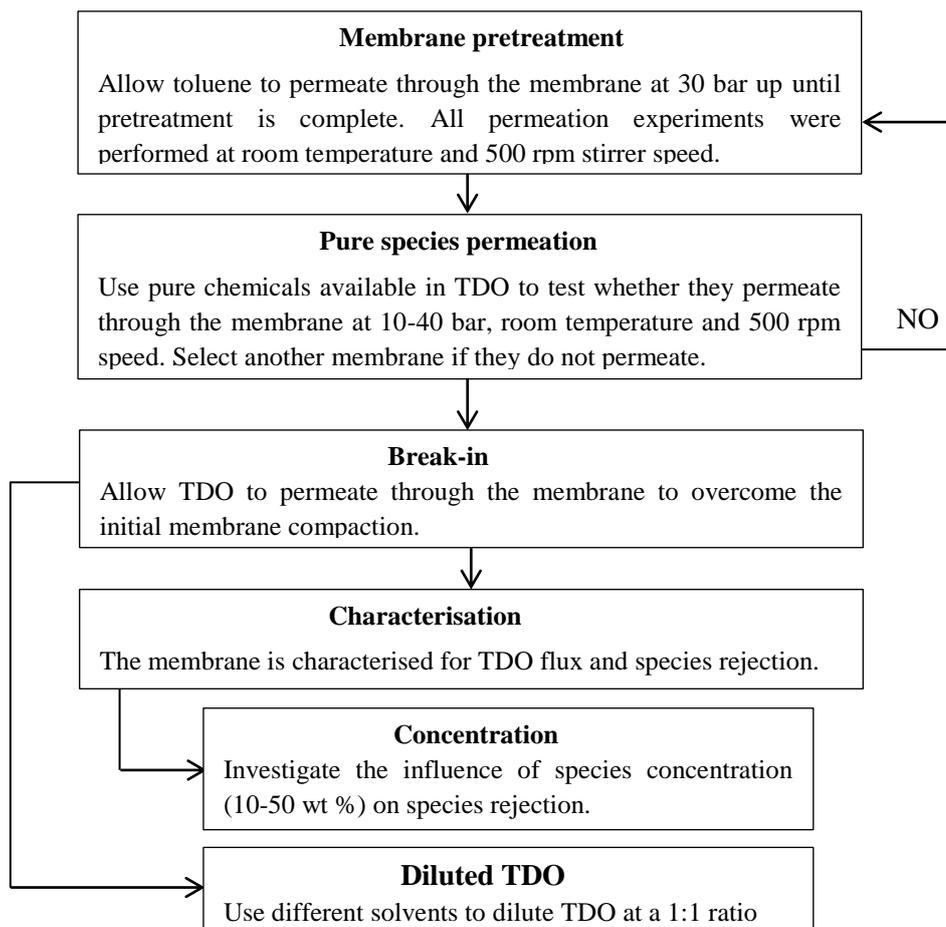


Figure 3.5: Experimental design followed in this study

All OSN experiments follow a standard procedure that is initiated by membrane pretreatment. Toluene was used as a pre-treating solvent for all filtration experiments. After pretreatment, the membrane must still overcome initial compaction that might occur through initial contact with the species to be characterised for flux and rejection. Membrane break-in is responsible for the latter.

Evonik OSN membranes are usable at pressures between 5-60 bar. To avoid membrane compaction and catastrophic equipment failure, the experimental work of this study was designed to only focus on a 10-40 bar pressure range.

TDO diluting solvents were selected on the basis of their solubility parameter. Amongst all the solvents (toluene, 1-octene and ethanol), ethanol has the strongest attraction for the membrane. According to literature (Postel *et al.*, 2013), a solvent with less affinity for the membrane influences negative rejections.

The effect of concentration on membrane performance (flux and rejection) was once studied by Darvishmanesh *et al.* (2011). This study also plans to investigate the effect of concentration on membrane performance. The concentration of TDO components was varied by blending crude TDO with certain pure species.

3.5.1: Manipulated variables

The results of all experiments in this study focused on permeate flux and species rejection which were determined and calculated according to procedures and equations described in Section 3.4. The manipulated variables of the present study include transmembrane pressure, membrane type, solvent type and species concentration. Table 3.5 summarises the selected variables of this study.

Table 3.3: Summary of experiments conducted and manipulated variables.

Experiment	Variable	Range
Pure species nanofiltration	Pressure	10 to 40 bar
TDO purification	Membrane type	PM-280, ST-280 and DM-200
	Membrane type	PM-280, ST-280 and DM-200
Diluted TDO purification	Solvent type	Toluene, 1-Octene and Ethanol
TDO purification	Species concentration	50×10^3 to 150×10^3 ppm

Studies (Scarpello *et al.*, 2002; Szekely *et al.*, 2014) have shown that the performance of the membrane is influenced by temperature. This study aimed at purifying TDO without the use of thermal energy. Hence the effect of temperature is not within the scope of the present study. All

nanofiltration experiments were conducted at room temperature (± 22 °C). The magnetic stirrer speed was also maintained at 500 rpm in all experiments.

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CHAPTER 4

Results and Discussion

4.1 Overview

Less sulphurous TDO and purified TDO components have numerous benefits in the petroleum and several chemical industries respectively. The potential benefits of TDO have not been fully accessed due to the difficulty that lies in the purification and chemical isolation steps. The most commonly used TDO purification method is distillation. Distillation consumes tremendous amount of energy and is not convenient in purifying limonene and reducing sulphur content. It is high time that alternative TDO purification methods are developed. The aim of this chapter is to show the capability of OSN membranes in purifying TDO.

This chapter is divided into 5 sections. Section 4.2 focuses on the analysis of TDO and presents the quantification of TDO components. Section 4.3 demonstrates the permeation of pure species through commercial OSN membranes. Section 4.3 also discusses the chemical and membrane properties responsible for separation. Section 4.4 demonstrates the potential of selected OSN membranes in purifying TDO. The membranes are characterised by their ability to retain specific TDO components and their ability to allow TDO permeation. Section 4.5 evaluates the purification of TDO via OSN and distillation.

4.2 TDO analysis

4.2.1 Introduction

Quantification of TDO components is key and fundamental for this study. Certain species present in crude TDO were quantified using procedures described in Section 3.3. Chemicals quantified were *dl*-limonene, *p*-cymene, 1,2,4-trimethylbenzene, toluene and benzothiazole. *dl*-limonene is a valuable species and this study aims for its purification/recovery. 1,2,4-trimethylbenzene and *p*-cymene were quantified because they share the same physical properties with limonene. The knowledge of how *p*-cymene and 1,2,4-trimethylbenzene behave under OSN is vital for the purification of limonene. Benzothiazole is an abundant sulphur species in TDO. Benzothiazole was quantified so as to track its reduction from TDO via OSN. The behaviour of the BTX fraction was represented by toluene.

Premium green fuel (Botriver, South Africa) also did analysis of specific relevant TDO properties such as viscosity, calorific value, flash point, water content, ash content and sulphur content.

4.2.2 Reproducibility and experimental error

The experimental error and reproducibility of the TDO quantification methodology described in Chapter 3 was tested to affirm reliability. Four samples were prepared and quantification experiments were conducted consecutively using the GC-FID instrument. A summary of the species quantification experimental error is presented in Table 4.1.

Table 4.1: Repeatability and experimental error of species quantification

Species	Concentration (ppm)	Standard Deviation(σ)	Error (%)
<i>dl</i> -Limonene	7833.78	574.23	7.33
p-Cymene	12523.97	967.47	7.72
1,2,4-trimethylbenzene	1430.94	112.15	7.84
Benzothiazole	3390.51	204.08	6.02
Toluene	10412.85	869.74	8.35

Table 4.1 clearly indicate that the TDO sampling and quantification method is sufficient. The two main target species analysis error is 7.33 % for limonene and 6.02 % for benzothiazole. The species concentration can be estimated with an average experimental error of 7.45%.

4.2.3 Characterisation of TDO

The market value of the TDO depends on the quantity of its components. Several researchers (Kyari *et al.*, 2005; Laresgoiti *et al.*, 2004; Ngxangxa, 2016) studied the quantification of TDO species. Table 4.2 compares the species quantification done in this study with that of Ngxangxa (2016).

Table 4.2: TDO species quantification

Species	Concentration (ppm)	
	This study	Ngxangxa (2016)
Limonene	8279.44	11800
p-cymene	12544.08	1290
1,2,4-trimethylbenzene	1423.57	1810
Toluene	10432.85	3030
Benzothiazole	3357.49	3810

It is clear from Table 4.2 that the quantity of limonene is less in this study's TDO compared to Ngxangxa (2016). It is also clear that the quantity of benzothiazole is comparable in both TDO's. The high concentration of p-cymene in this study's TDO is due to the instruments inability to separate p-cymene from m-cymene and o-cymene. Ngxangxa (2016) used a GC-MS capable of isolating closely related compounds.

The concentration of TDO species is dependent on several pyrolysis operating parameters. Amongst others, temperature, heating rate, residence time and presence of a catalyst are labelled as the most influential on species concentration (Nkosi and Muzenda, 2014).

The study of Pakdel *et al.* (2001) pointed out that the concentration of limonene is highly dependent on temperature, residence time and pressure. Pakdel *et al.* (2001) also highlighted that limonene

decomposes to isoprene and aromatic compounds such as trimethylbenzene, cymene and indane at temperatures above 450 °C.

The fuel nature of TDO lies in its physical properties. Several researchers (Sebola *et al.*, 2013; Pilusa *et al.*, 2017) studied the fuel properties of TDO. The data presented in Table 4.3 compares the physical properties of different TDO's with the fuel properties as per South African National Standards (SANS 342).

Table 4.3: Fuel properties of different TDO's relative to SANS specifications.

Property	This study	TDO-1	TDO-2	SANS-342
Energy (MJ/kg)	44	43	39.9	-
Viscosity (cSt)	3.88 @ 25°C	9 @ 40°C	9.23 @ 40°C	2.2-5.3 @ 40°C
Sulphur (ppm)	5300	9106	11450	<500
Density @ 20°C (kg/m ³)	905.3	926	942	800-950
Water	<0.1 mass%	3.54 vol%	33540 mg/kg	<0.04 vol%
Flash point (°C)	25°C	94°C	96°C	>55

*: TDO-1: Sebola *et al.*, 2013; TDO-2: Pilusa *et al.*, 2017

It is clear from Table 4.3 that the sulphur content of all TDO solutions is high above the maximum amount specified by SANS 342. In TDO, sulphur basically exists in organic forms as mercaptants, thiophenes and sulphides (William, 2013). Besides the negative environmental impact that high sulphur levels present, studies (Martinez *et al.*, 2014) have shown that high sulphur content cause corrosion of the engine components.

Mercaptants are the only sulphur components in TDO that boil below 100°C. Pilusa *et al.* (2017) and Sebola *et al.* (2013) demonstrated that mercaptants can be easily removed from TDO by gas-phase desulphurization distillation. Other sulphur components such as benzothiazole's have high boiling points and high molecular weights. Reducing the high boiling sulphur species via distillation also reduces the vital aromatic compounds responsible for lubricating the engine components. Rodriguez *et al.* (2014) reported that the removal of sulphur and nitrogen compounds reduces the natural lubricity of the oil.

Benzothiazole's content in this study's TDO accounts for approximately 60% of the overall sulphur content. This implies that mercaptants and other sulphur species are minor in this study's TDO. Reducing 50-60% of benzothiazole will be a major achievement in the field of TDO desulphurization.

The TDO obtained from premium green fuel has fuel properties comparable to that specified by SANS. Besides flash point, other properties such as energy, density and viscosity are near the

properties of fuels as per SANS 342. Low flash points are associated with potential risks of auto ignition during storage.

4.2.4 Concluding remarks

TDO was characterised using methods described in Section 3.3. The species quantification methods used were justified by comparing the species concentration of this study with that of previous publications. The fuel nature of the TDO was discussed relative to SANS 342 specifications. The TDO used in this study had a low sulphur content compared to other TDO's used in literature. 60% of the total sulphur content in the TDO was represented by benzothiazole.

4.3 OSN: Pure species

4.3.1 Introduction

Separation through a membrane is based on the difference in the rate at which chemicals permeate. Various physical properties of chemicals are influential to the flux of species across membranes. Molecular weight, viscosity and parameters describing species-membrane interaction have been identified as the most influential properties in species permeation (Bhanushali *et al.*, 2001). Other properties such as dipole moment and surface tension also play a role in separation through a membrane. The flux of pure species was estimated using Equation 2.1 (Saravanan *et al.*, 2006).

$$J = \frac{V}{A \times t} \quad (2.1)$$

Where

J is the flux (L.m⁻².h⁻¹)

V is the volume of collected permeate (L)

A is the active surface area (m²)

t is the time (h)

This section demonstrates the potential of OSN membranes in separating molecules of closely related physical properties. 1,2,4-trimethylbenzene, p-Cymene and indane are all aromatic compounds whereas limonene is classified as a terpene. Such differences play huge roles in separation across membranes. OSN membranes that fail to allow permeation of pure molecules were considered not feasible or incapable of purifying TDO. Pure species permeation was considered as membrane screening for this study.

4.3.2 Reproducibility and experimental error

The reproducibility and experimental error of the OSN methodology described in Section 3.4 was tested by consecutively performing at least 3 experimental runs for each pure component (Limonene,

p-cymene, 1,2,4-trimethylbenzene and toluene). The experiments were conducted at different operating conditions (10-40 bar). Table 4.4 summarises the pure species experimental error.

Table 4.4: Experimental errors of pure species flux through PM-280

Pressure (bar)	Flux (L.m ⁻² .h ⁻¹)	Standard deviation (σ)	Error (%)
Limonene			
10	25.1	2.52	10.20
20	54.3	1.52	2.81
30	75.0	3.61	4.74
40	92.4	3.05	3.42
p-cymene			
10	44.3	2.65	6.29
20	92.0	1.15	1.25
30	141.1	7.37	5.33
40	168.0	4.16	2.46
1,2,4-trimethylbenzene			
10	40.3	1.52	3.85
20	72.4	3.51	4.90
30	108.7	3.61	3.35
40	120.2	4.36	3.54
Toluene			
10	95.5	2.65	2.84
20	190.3	8.32	4.32
30	297.8	4.73	1.60
40	372.6	3.05	0.82

The OSN methods described in Section 3.4 were validated for reproducibility. The pure species flux values can be approximated with an average experimental error of 3.85 %. Other publications (Van der gryp *et al.*, 2010; Peddie *et al.*, 2016) reported an experimental error of approximately 3.0 % for pure species.

4.3.3 Pure species permeation results

This section presents the permeation performance (pure species flux) of PM-280, ST-228 and DM-200. The effect of transmembrane pressure and species physical properties is examined with respect to pure species flux. Table 4.5 and Figure 4.1 presents the pure species flux of limonene, p-cymene, 1,2,4-trimethylbenzene and toluene at different transmembrane pressures.

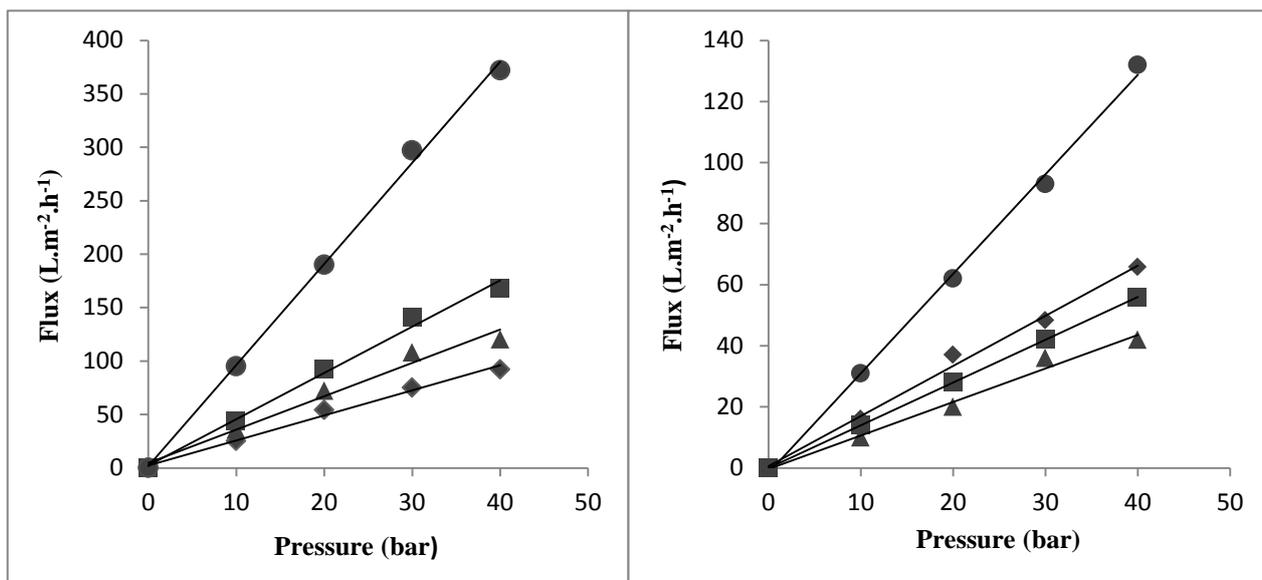


Figure 4.1: Effect of pressure on pure species flux through PM-280 (left) and ST-228 (right)

[Limonene ◆ ; p-Cymene ■ ; 1, 2, 4-Trimethylbenzene ▲ ; Toluene ●]

It is clear from Figure 4.1 that the flux of a species increases with increasing transmembrane pressure (10-40 bar). In ascending order, the pure species flux through PM-280 can be arranged as limonene < 1,2,4-trimethylbenzene < p-cymene < toluene. The relationship demonstrated in Figure 4.1 is easily explained by Equation 4.1 (Adam *et al.*, 1983).

$$J_v = L_p(\Delta p - \sigma \Delta \pi) \quad (4.1)$$

J_v : Volume flux

L_p : Membrane permeance

Δp : Transmembrane pressure

σ : Reflection coefficient

$\Delta \pi$: Osmotic pressure difference

Equation 4.1 describes that the volume flux of a specific solute across a membrane in the absence of osmotic pressure ($\Delta \pi \cong 0$) is linear to the transmembrane pressure (Adam *et al.*, 1983). Several other studies (Darvishmanesh *et al.*, 2011; Bhanushali *et al.*, 2001; Gibbins *et al.*, 2002) reported the same linear relationship between flux and pressure. L_p describes the permeance of a species through the membrane. Table 4.5 presents the unique L_p values of each species.

Table 4.5: Membrane permeance of pure species

Species	L_p (L.m ⁻² .h ⁻¹ .bar ⁻¹)		
	PM-280	ST-228	DM-200
Limonene	2.5	1.6	-
p-cymene	4.7	1.4	-
1,2,4-trimethylbenzene	3.6	1.2	-
Toluene	9.9	3.1	-
Benzothiazole	-	-	-

It can be observed from Table 4.5 that pure species permeate with more ease through PM-280. Both PM-280 and ST-228 have a MWCO of 280 g/mol and are fabricated with Lenzing P84. PM-280 achieved higher permeances because its structure is modified by the manufacturer to optimise the transport of non-polar molecules.

One interesting observation that can also be seen from Table 4.5 is that the permeance of benzothiazole could not be estimated through all three membranes. The PM-280 and ST-228 membranes were not stable against pure benzothiazole. Benzothiazole contains a very polar bond formed by nitrogen and hydrogen (N-H Nitrogen). Nitrogen is one of the most electronegative atoms. Its union with hydrogen results in a polar bond that dissolves hydrophobic membranes.

It can also be observed from Table 4.5 that all species failed to permeate through DM-200. DM-200 has a MWCO of 200 g/mol and its structure is modified by the manufacturer to optimise the transport of polar molecules. All chemicals listed in Table 4.5 are considered as non-polar. The polar nature of the DM-200 membrane and the non-polar nature of the molecules repel each other. The MWCO of DM-200 is also small relative to the molecular weights of limonene, p-Cymene and trimethylbenzene. Smaller pores restrict permeation of molecules.

Through PM-280, p-cymene permeates 1.88 times faster than limonene, while 1,2,4-trimethylbenzene permeates 1.44 times faster than limonene. The permeation of limonene through PM-280 and ST-228 is very comparable to that of p-cymene and 1,2,4-trimethylbenzene. The close relation between the permeance of limonene and limonene-like impurities is a major setback for the purification of limonene through OSN.

The difference in permeance arises from species physical properties and membrane properties. Previous studies (Lutze and Gorak, 2013; Bhanushali *et al.*, 2001) have demonstrated that the permeance of a pure species depends on the species physical properties (molecular weight, viscosity, geometry, polarity, dipole moment, surface tension, charge and solubility parameter) and membrane

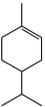
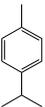
properties (MWCO, polarity, solubility parameter and crosslinking). To discuss the permeation differences of pure species, species properties are listed in Table 4.6.

The large flux difference between toluene and other species was anticipated due to the small molecular weight of toluene (92.14 g/mol) relative to the molecular weight cut-off of both the PM-280 and ST-228 membranes. The small size of toluene enabled easier permeation across the membranes. Limonene (136.24 g/mol), p-Cymene (134.21 g/mol) and 1,2,4-Trimethylbenzene (120.19 g/mol) have closely related molecular weights and geometry. When arranging the molecules in order of increasing molecular weight, toluene < 1,2,4-trimethylbenzene < p-Cymene < limonene, no clear relationship is noticed between volume flux and molecular weight. The missing correlation is a direct indication that the flux of a species is not only dependent on the molecular weight of a species.

Viscosity is one of the species physical properties that have been reported to greatly influence the transport of molecules across membranes (Aerts *et al.*, 2006; Dijkstra *et al.*, 2006; Bhanushali *et al.*, 2001). Limonene, p-Cymene and 1,2,4-trimethylbenzene all have a viscosity of approximately 1 mPa.s. The viscosity similarity is a major set-back in the purification of limonene by OSN membranes. When arranging in order of increasing viscosity, the order is presented as 1,2,4-trimethylbenzene < p-cymene < limonene. From the order, it can be seen that p-cymene and 1,2,4-trimethylbenzene swapped places when comparing with the order of increasing flux. It is clear that the slight difference in viscosity of pure species is bringing about a negligible difference on species flux.

The dipole moment of limonene, p-cymene and 1,2,4-trimethylbenzene perfectly explains the permeation across PM-280 membrane. Ebbing and Gammon (2009) defined dipole moment as a measure of bond polarity. A molecule with an overall dipole moment of zero is considered non-polar. When arranging the molecules in order of increasing dipole moment, p-cymene < 1,2,4-trimethylbenzene < limonene, a clear correlation is noticed between polarity and volume flux. PM-280 is a hydrophobic membrane that is modified to ideally transport non-polar molecules. The most non-polar molecule is expected to have a high flux through PM-280 because of the strong attraction between the membrane and the molecule. P-cymene is the most non-polar molecule (0 D) and as a result its flux is higher than that of limonene and 1,2,4-trimethylbenzene. This shows that the dipole moment of a species is inversely proportional to the membrane's permeation performance.

Table 4.6: Properties of species used in this project

Chemical	MW (g/mol)	Shape	Boiling Point (°C)	Viscosity (mPa.s ⁻¹)	Dipole Moment (D)	Surface Tension (mN/m)	Solubility parameter (MPa ^{0.5})
Limonene	136.3		176	1.01	1.570	26.75	16.4
p-Cymene	134.2		177	0.937	0.000	28.35	17.4
1,2,4-trimethylbenzene	120.2		171	0.925	0.300	29.19	18.2
Toluene	92.1		110.6	0.645	0.360	27.93	17.8
Benzothiazole	135.2		228	6.56	1.460		24.2

The direct correlation between dipole moment and flux demonstrates the importance of species-membranes interactions, i.e. mutual affinity between membrane and permeating species. Dipole moment alone is also not sufficient to explain the transport of molecules.

Solubility parameter difference is another property that accounts for the mutual affinity between two species. Equation 4.2 is used to estimate the difference in solubility parameters ($\Delta\delta$) between two species. The respective solubility parameters of different species were estimated using the group contribution method that is highly considered as accurate and reliable (Fedors, 1974; Hansen, 2007; Van Krevelen and Te Nijenhuis, 2009).

$$\Delta\delta = | \delta_i - \delta_{p84} | \quad (4.2)$$

Where:

δ_i : Solubility parameter of species

δ_{p84} : Solubility parameter of membrane material, i.e. Lenzing p84 is 27.1 MPa^{0.5}

The difference in solubility parameters is used to estimate the mutual affinity of two species toward each other (Seroko *et al.*, 2011). The mutual affinity between two species is stronger when the solubility parameter difference is lower. A stronger mutual affinity between a membrane material and a particular species results in a high flux/permeance. This mutual relationship between permeance and solubility parameter difference is also justified in literature (Seroko *et al.*, 2011; Robinson *et al.*, 2004).

The solubility parameter difference between Lenzing p84 and limonene is higher than that of p84/p-Cymene and p84/1,2,4-trimethylbenzene. As a result of the weak interaction between limonene and lenzing p84, limonene has the lowest permeance through PM-280. However, when arranging in order of increasing solubility parameter difference, 1,2,4-trimethylbenzene < p-Cymene < Limonene, a clear correlation with permeance is unclear. The solubility parameters of limonene, p-cymene and 1,2,4-trimethylbenzene are closely related, 16.4 MPa^{0.5}, 17.4 MPa^{0.5} and 18.2 MPa^{0.5} respectively. The small difference between the respective solubility parameters is causing a negligible difference on the flux of the pure species. As a result, solubility parameter difference cannot be used in this case to formulate a model of predicting the flux.

Surface tension is also another parameter that accounts for the mutual affinity between two species. The surface tension of limonene, p-Cymene and 1,2,4-trimethylbenzene is approximately equal 28 mN/m leading to difficulties in separation and prediction.

Previous studies (Bhanushali *et al.*, 2001; Geens *et al.*, 2007) reported that a good flux model is a combination of species viscosity, molecular size and a parameter describing the mutual affinity

between a species and a membrane (polarity, solubility parameter difference, surface tension etc.). Bhanushali *et al.* (2001) proposed a flux model as presented in Equation 4.3.

$$Flux \propto \left(\frac{molecular\ size}{1}\right) \times \left(\frac{1}{viscosity}\right) \times \left(\frac{1}{affinity}\right) \quad (4.3)$$

Equation 4.3 provides a good correlation with the fluxes of pure species (Limonene, p-cymene, 1,2,4-trimethylbenzene). Figure 4.2 confirms the influence of molecular size, viscosity and species-membrane interaction on species flux. Separation and flux prediction of molecules weighing between 100 – 300 g/mol remains a challenge in the field of OSN because of the similarity in species physical properties.

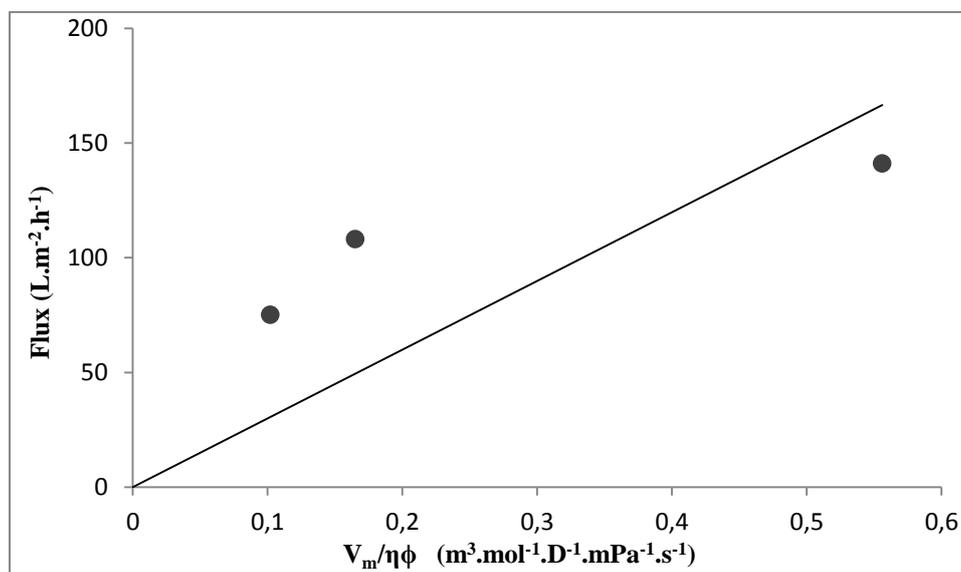


Figure 4.2: Confirmation of influence of molecular size, viscosity and species-membrane affinity on species flux.

4.3.4 Concluding remarks

The permeation of pure components was characterised by different OSN membranes, i.e, PM-280, ST-228 and DM-200. A linear relationship between the transmembrane pressure and volume flux/permeance was demonstrated. Results also showed that permeation of molecules is dependent on the inverse of species dipole moment. As the dipole moment of a species increases, the flux decreases. The individual contribution of viscosity, solubility parameter and surface tension on flux could not be justified due to the close relation of the physical properties of pure species. The flux model proposed by Bhanushali *et al.* (2001) confirmed the influence of molecular size, viscosity and species-membrane affinity on membrane permeation performance.

Separation of limonene via OSN from limonene-like impurities seems to be experiencing the same challenge that distillation experiences, similarity in species physical property. Through PM-280, the flux of p-cymene is only 1.88 times higher than that of limonene while the flux of 1,2,4-

trimethylbenzene is 1.44 times higher than that of limonene. Since separation/purification through a membrane depends on the rate at which components permeate, the separation of limonene via OSN is uncertain/doubtful.

4.4 TDO purification by OSN

4.4.1 Introduction

It is preferred in this study that limonene and other light molecules permeate through the membrane in high concentrations. At the same time, it is preferred that the membrane rejects high molecular weight compounds and other impurities such as sulphur compounds. The potential of OSN membranes in purifying TDO was tested by rejection studies described in Section 3.4.2.3. Species rejection was estimated using Equation 2.2 (Saravanan *et al.*, 2006).

$$R = \left(1 - \frac{c_p}{c_f}\right) \times 100\% \quad (2.2)$$

Where

c_p Is the concentration of the solute in the permeate stream (mg/L)

c_f Is the concentration of the solute in the feed stream (mg/L)

The membrane's TDO permeation and species rejection performance is characterised and discussed in this section. The transmembrane pressure and rotation speed were kept constant at 30 bar and 500 rpm respectively in all experiments. The effect of solvent dilution and species concentration on membrane performance is also discussed.

4.4.2. Experimental results

The experimental results obtained after processing Crude TDO by PM-280, ST-228 and DM-200 membrane are presented in Table 4.7 and Table 4.8. The transmembrane pressure and stirrer rotation speed were kept constant at 30 bar and 500 rpm respectively.

Table 4.7: TDO flux through commercial OSN membranes

Membrane	TDO Flux ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$)
PM-280	0.877
ST-228	-
DM-200	-

Table 4.8: Rejection performance of PM-280 after crude TDO filtration at 30 bar.

Species	Rejection (%)
Limonene	-7
p-cymene	-11
1,2,4-trimethylbenzene	-2
Toluene	-15
Benzothiazole	-6

It is clear from Table 4.7 that crude TDO failed to permeate through ST-228 and DM-200. The steady volume flux achieved by PM-280 for crude TDO is $0.877 \text{ L.m}^{-2}.\text{h}^{-1}$. Through PM-280, the volume flux gradually decreased with time to a point of zero permeation ($> 5\text{hr}$). An acceptable explanation for the zero permeation recorded with ST-228 and the low to zero flux recorded with PM-280 is concentration polarization. Jaffrin (2015) defined concentration polarization as a phenomenon whereby macromolecules form a layer on the surface of a membrane, creating resistance to permeating components of the feed solution. Vandezande *et al.* (2008) added that concentration polarization will ultimately lead to a reduction in permeate flux. TDO is concentrated with all kinds of molecules capable of influencing concentration polarization, for example, heavy, branched, long chained and molecules of different polarities. Such molecules block the permeation of low sized molecules and other molecules having the ability to permeate

To prove that the apparent results were due to concentration polarization and not membrane fouling, the PM-280 membrane used for TDO purification was re-used to process pure toluene. Toluene permeated at the same flux ($297 \text{ L.m}^{-2}.\text{h}^{-1}$) recorded before the membrane was subjected to TDO purification. This shows that the membrane preserved its separation characteristics and is stable with TDO.

Low fluxes are bound to result in poor separation of components. The use of a more porous (high MWCO) membrane can reduce concentration polarization and increase the TDO flux. A more porous membrane will also reduce the selectivity of the TDO components as heavy and chained molecules will also be permeating through the membrane with ease.

It is clear from Table 4.8 that the rejection of TDO components is negative through PM-280 membrane. A negative rejection of a specific solute means that the solute is more concentrated in the permeate than the feed. A negative rejection is also an indication of the separation of TDO components. When the membrane retains heavy molecules while allowing smaller molecules to permeate, the concentration of the low molecular weight compounds is increased in the permeate resulting in a negative rejection. Filippov *et al.* (2017) obtained negative rejections for nanionic dyes during nanofiltration by hydrophobic membranes. Filippov *et al.* (2017) explained that the negative

rejection implies that the dye concentrates on the permeate side because of positive adsorption of the neutral dye molecules inside the membrane pores.

In this study, a negative rejection close to zero is considered as a low negative rejection. Low negative rejections are not a satisfying result since they imply that the concentration of the species in the permeate is just slightly higher than the concentration in the feed solution. However, negative rejections show the possibility of recovering target compounds or low molecular weight compounds from crude TDO via OSN.

In literature (White and Nitsch, 2000), vegetable crude oils are sometimes dewaxed by nanofiltration membranes. In previous publications (Darvishmanesh *et al.*, 2011; White and Nitsch, 2000), the flux of crude vegetable oil diluted with solvents ranges from 4-56 L.m⁻².h⁻¹ depending on the nature of the solvent and membrane. This study wishes to dilute TDO to enhance the flux and separation of TDO components.

4.4.3 Dilution of feed solution

4.4.3.1 Introduction

Postel *et al.* (2013) used different solvents to enhance the transport of solutes across a membrane. The study showed that a solvent with less affinity for the membrane influences negative rejections of the solutes. A low solubility parameter difference between two materials was considered as a strong mutual affinity between the particular materials. The strong mutual affinity between the membrane and solute was also labelled as an influencing parameter for negative rejections. Postel *et al.* (2013) concluded by highlighting that negative rejections are possible if the solute is preferably dissolved in the membrane material.

In this section, the effect of three solvents is evaluated and discussed. Crude TDO was diluted with toluene, 1-octene and ethanol. The three solvents were selected on the basis of solubility parameter, i.e. solvent/membrane affinity. Ethanol has the strongest affinity for the membrane while 1-octene has the weakest. Table 4.8 presents the physiochemical properties of the solvents used.

Table 4.8: Physiochemical properties of solvents used to dilute TDO.

Solvent	Molecular weight (g/mol)	Solubility parameter (MPa ^{0.5})	Viscosity (mPa.s ⁻¹)	Dipole moment (D)	Surface Tension (mN/m)
Toluene	92.1	17.8	0.645	0.360	27.93
1-Octene	112.2	15.64	0.447	0.340	21.29
Ethanol	46.07	25.42	1.057	1.690	23.39

4.4.3.1 Experimental results and discussion

The ST-228 membrane was used to study the effect of TDO dilution at 30 bar and 500 rpm. The ST-228 was selected for this study because it allowed the permeation of pure species and not of TDO. The experimental results obtained for TDO dilution by different solvents are presented in Figure 4.3 and Table 4.9.

It is clear from Figure 4.3 that the flux of crude TDO is improved by solvent dilution. Initially crude TDO did not permeate through ST-228. The flux of the TDO/solvent solution is highly dependent on the flux of the pure solvent. The TDO/toluene flux is 7.8% the flux of pure toluene, TDO/1-octene flux is 3.5% the flux of pure 1-octene and the flux of TDO/ethanol is 7.7% the flux of pure ethanol.

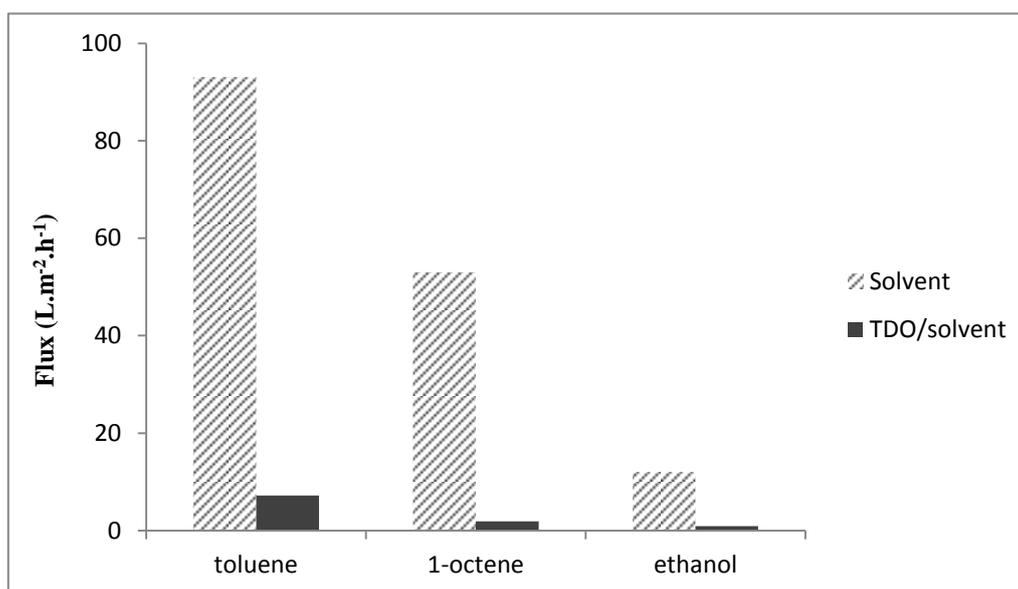


Figure 4.3: Effect of solvent dilution on TDO flux

Table 4.9: Effect of solvent dilution on species rejection

Species	Rejection (%)		
	TDO/toluene	TDO/1-Octene	TDO/ethanol
Limonene	-10.2	18.0	3.4
p-cymene	-22.5	15.4	3.2
1,2,4-trimethylbenzene	-64.3	12.6	5.2
Benzothiazole	-98.0	9.4	2.7

It is clear from Table 4.9 that the permeation of TDO components is influenced most when toluene is used to dilute TDO. TDO/toluene solution produced negative rejections for all characterised TDO

components. The results on Table 4.9 also show that a better TDO flux enhances the permeation of TDO components.

When arranging in order of increasing solute rejection, TDO/toluene < TDO/ethanol < TDO/1-octene, a clear correlation between solvent/membrane mutual affinity and solute rejection is missing. According to Postel *et al.* (2013), purification of TDO/1-octene should have resulted in the lowest solute rejections because the membrane has less or no affinity for 1-octene.

TDO/Ethanol achieved lower solute rejections than TDO/1-octene despite its strong affinity for the membrane. The ethanol permeate solution was hard to sample due to its existence as a two liquid phase solution. The two phases are an indication that most TDO components did not dissolve in ethanol. Ethanol is a polar solvent having less affinity for hydrophobic membranes and solutions. Its polarity accounts for the low TDO/ethanol flux ($0.93 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) and the multilayer permeate.

It can be observed from Table 4.9 that benzothiazole achieved the lowest rejections in all three solvents. Benzothiazole has the strongest affinity for the membrane. The strong mutual affinity between benzothiazole and the membrane makes it convenient for benzothiazole to permeate and increase its concentration on the permeate side, resulting in a low or even negative rejection. In fact, a clear correlation is noticed between solute rejection and solute/membrane solubility parameter difference. The stronger the mutual affinity between the solute and the membrane, the lower the rejection. TDO/toluene and TDO/1-octene solutions demonstrated this correlation, as illustrated in Figure 4.4.

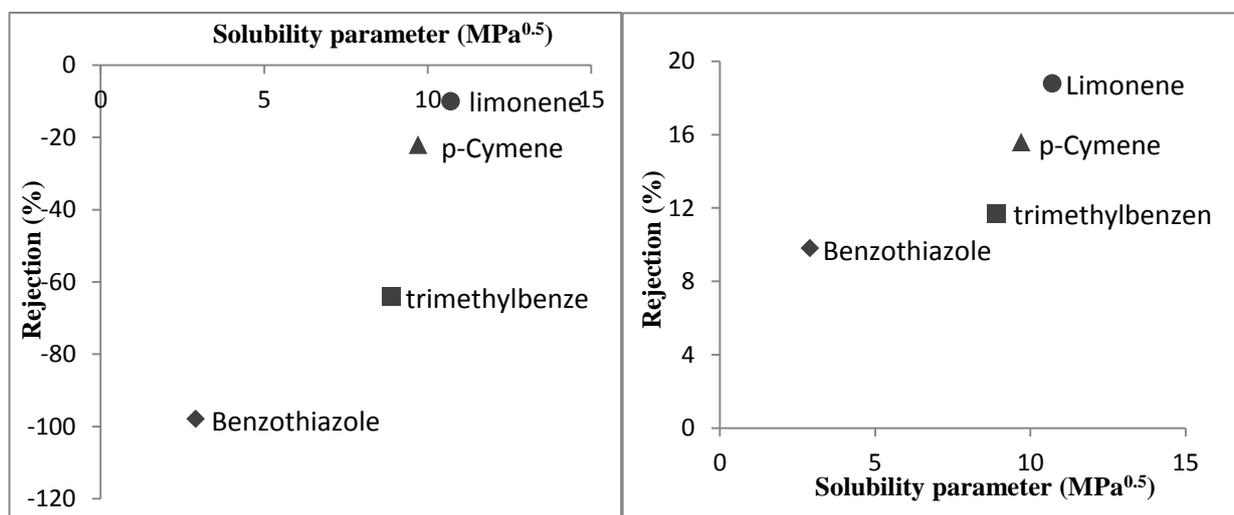


Figure 4.4: Correlation between the rejection of TDO species and species/membrane mutual affinity.

It can be seen from Figure 4.4 that the permeation of diluted TDO species is influenced by the mutual affinity between the membrane and the species. The study of Postel *et al.* (2013) also emphasizes that negative rejections are possible if the solute is preferably dissolved in the membrane material.

4.4.4 Effect of concentration on membrane rejection performance

4.4.4.1 Introduction

Several researchers (Scarpello *et al.*, 2002; Whu *et al.*, 2000) have reported that high solute concentrations decrease the total flux of the feed solution. Concentration polarization is an acceptable explanation for the decline in flux. Few publications (Darvishmanesh *et al.*, 2011) report the effect of species concentration on membrane rejection performance.

In future, one possible way of investigating the purification of TDO via OSN will involve using a post-distillation TDO stream as the feed. A post-distillation TDO stream already has an improved limonene concentration. This section aims to investigate the effect of species concentration on membrane rejection performance. The species concentration in TDO was increased by adding the pure form of the particular species. The ST-228 membrane was used at 30 bar and 500 rpm rotation speed.

4.4.4.2 Experimental results and discussion

Figure 4.5 presents the experimental results for the effect of TDO species concentration on membrane (ST-228) rejection performance. Pressure and stirrer rotation speed were kept constant at 30 bar and 500 rpm respectively.

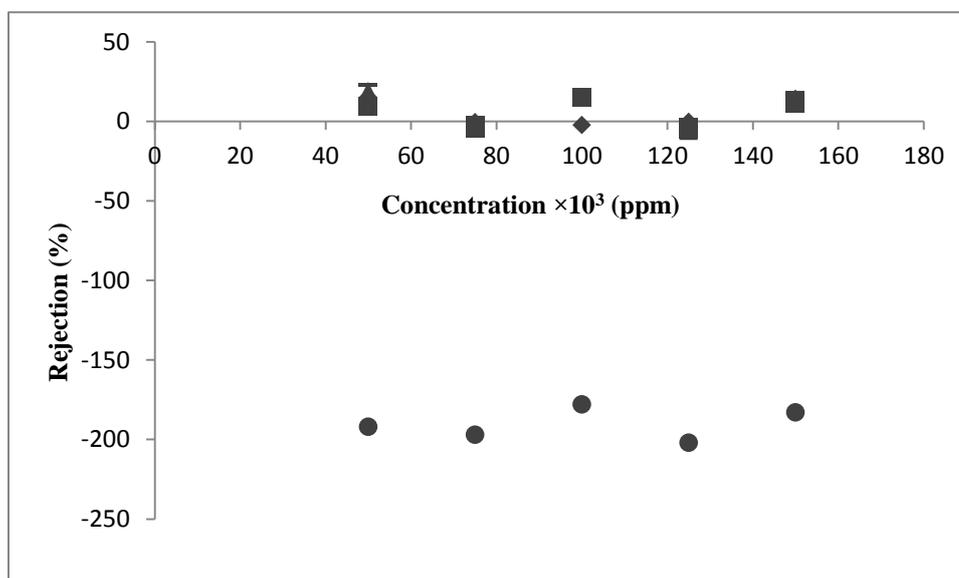


Figure 4.5: Effect of species concentration on membrane performance [Limonene ◆; p-Cymene ■ ; 1, 2, 4-Trimethylbenzene ▲ ; Toluene ● ; Benzothiazole ▬]

It is clear from Figure 4.5 that species concentration has no significant effect on membrane rejection performance. The work of Darvishmanesh *et al.* (2011) also confirms that species concentration has no effect on species rejection. This result implies that the species rejection values seen in this study will be comparable to that obtained after using a post-distillation TDO stream as the feed solution.

However, a post-distillation TDO stream will reduce concentration polarization and improve the overall separation of TDO species.

4.4.5 Concluding remarks

The PM-280, ST-228 and DM-200 resulted in high TDO rejections, 88%, 100% and 100% respectively. It was anticipated that both PM-280 and ST-228 membranes will at least fractionate the TDO into a heavy and a light fraction. Concentration polarization was deduced as an explanation for the high TDO rejections. TDO purification through PM-280 resulted in negative rejections for limonene and benzothiazole, -6% and -7% respectively. The high TDO rejection and high species rejection mean that the transport of TDO through the membrane is restricted.

The dilution of TDO with different organic solvents was effective in increasing permeation of TDO through OSN membranes. The anticipated fractionation and permeation of target compounds was still unsatisfactory. After diluting TDO with toluene, several solutes achieved negative rejections implying that they are more concentrated on the permeate side than the feed solution. About 15% of limonene was recovered in the permeate solution. Benzothiazole's overall reduction was approximately 6%. Even with dilution, the membrane still recovers less than 20% of limonene which implies that the permeation of TDO components is still restricted.

The study of the effect of solute concentration on membrane performance demonstrated that membrane rejection is independent of solute concentration.

4.5 Evaluation of OSN technology compared to distillation

4.5.1 Introduction

The recovery of valuable compounds from crude TDO is mostly studied using distillation. Compounds such as limonene are only marketable at purities greater than 95 wt%. Limonene purification by distillation is hindered by the presence of limonene-like impurities in TDO. Through distillation, compounds such as p-cymene, trimethylbenzene and indane concentrate on the limonene enriched fraction because of the comparable boiling points (~176 °C). Researchers such as Stanciulescu and Ikura (2006) mentioned that limonene isolation by ordinary distillation is impossible and only a limonene enriched fraction is possible.

Per SANS 342 specifications, TDO must contain a sulphur concentration of less than 500 ppm. Desulphurization of TDO is also widely studied through distillation.

This chapter's aim is to compare the purification of TDO via OSN with the purification of TDO via traditional techniques, mainly distillation.

4.5.2 Comparison

The data presented in Figure 4.6 compares TDO purification by OSN with TDO purification by distillation and other methods.

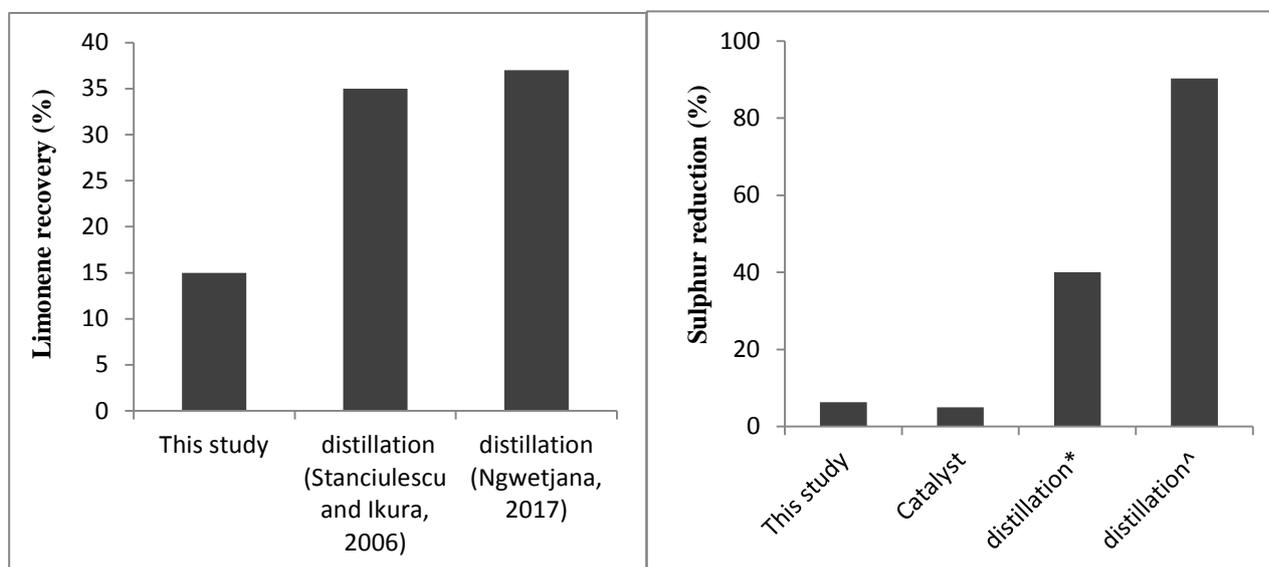


Figure 4.6: Limonene recovery and sulphur reduction from TDO [*: Sebola *et al.* (2013); ^: Pilusa *et al.* (2017); Al-MCM-48: Trongyong and Jitkarnka (2015)]

It is clear from Figure 4.6 that distillation has achieved the most in the field of limonene recovery from crude TDO. Ngwetjana (2017) conducted a TDO fractionation experiment using a single stage batch distillation set-up. The limonene enriched fraction contained a limonene content of 37 wt%. Stanciulescu and Ikura (2006) obtained a comparable limonene content of 32-37 wt% using a single batch distillation set-up.

Pakdel *et al.* (2001) obtained an improved limonene content of 55 wt% using a packed column with 25 theoretical stages.

The limonene enriched fraction of experiments conducted by Ngwetjana (2017), Stanciulescu and Ikura, (2006) and Pakdel *et al.* (2001) contained compounds of close boiling points such as indane, cymene's and trimethylbenzene's. Compounds having the same boiling point cannot be separated by a single batch distillation set-up.

Ngwetjana (2017) also simulated (Aspen Plus[®] V8.2) the recovery of limonene from limonene-like compounds using extractive and azeotropic distillation. A variety of entrainers such as diethylene glycol, triethylene glycol, quinolone, etc. were selected for the process models. The study showed that it is possible via extractive and azeotropic distillation to recover limonene at purities higher than 98 wt%.

The recovery of limonene via OSN was investigated in this study. The permeation of pure limonene through OSN membranes was found to be comparable to that of limonene-like compounds. The comparable permeation rates imply that the limonene enriched fraction obtained through OSN also contain limonene-like impurities.

Purification of diluted TDO through OSN resulted in a limonene recovery of approximately 15%. The limonene concentration in the feed and permeate solution was used to estimate the overall limonene recovery (Appendix B.4). Purification of crude TDO using PM-280 membrane resulted in a limonene recovery of 5%. It is clear from the limonene recovery results that a high TDO flux improves purification of TDO components.

It is also clear from Figure 4.6 that distillation procedures are currently leading in the field of TDO desulphurization. Sebola *et al.* (2013) achieved a 40% sulphur reduction by conducting a gas-phase desulphurization distillation at 250°C over membrane sieves. The study showed that the distilled TDO contains fuel properties comparable to commercial diesel. However, the distilled TDO did not meet the fuel specifications per SANS 342 because of the high sulphur content (> 4055 ppm).

Pilusa *et al.* (2017) conducted an oxidative gas-phase fractional distillation over 13× molecular sieves and achieved a 90.3% sulphur reduction. The study discussed that a fraction of sulphur species in TDO known mercaptants boils at temperatures below 100 °C, simplifying their removal from crude TDO through gas phase desulphurization distillation. Sulphides such as benzothiazole have larger molecular weights and high boiling points. Distillation at high temperatures is not advisable since aromatic compounds and other compounds responsible for the oil's viscosity and lubricity boils at high temperatures. The final TDO stream of the study of Pilusa *et al.* (2017) had a sulphur concentration of 1100 ppm which is higher than recommended by SANS 342 (< 500 ppm).

The purification of TDO via OSN achieved a 6.3% benzothiazole reduction. The OSN process was conducted by a ST-228 hydrophobic membrane at 30 bar operating pressure and 500 rpm. A 6.3% reduction is not sufficient in terms of meeting the SANS limit of less than 500 ppm. Since this study only focused on benzothiazole, the benzothiazole concentration (1683.2 ppm) alone is still well above 500 ppm. The study of Trongyong and Jitkarnka (2015) achieved a 5.0% sulphur reduction using an aluminosilicate MCM-48 catalyst during pyrolysis. The results also showed that the catalyst promotes ring-opening of PAHs and aromatization of cyclic compounds.

Desulphurization is key on the push for a less sulphurous TDO. Gas-phase desulphurization distillation is currently the leading technique in the field of TDO desulphurization.

4.5.3 Concluding remarks

This section compared the purification of TDO via OSN, distillation and other known methods. It was found in available literature that much progress has been made via distillation. Through gas-phase desulphurization distillation, Sebola *et al.* (2013) and Pilusa *et al.* (2017) managed to reduce 40% and 90% of total sulphur in TDO respectively. OSN managed to reduce 6.3% of benzothiazole in TDO. Up to date, no method has been able to meet the sulphur content requirements set by SANS 342.

Purification of crude and diluted TDO via OSN produced 5% and 15% limonene recoveries respectively. Limonene recovery through a single stage distillation set up results in concentrations between 32-37 wt%. Re-distillation of the limonene enriched fraction increases the limonene concentration to approximately 55 wt%. At concentrations lower than 95 wt%, limonene is not marketable. The comparison of TDO purification showed that a breakthrough is likely to come through distillation.

4.6 References

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CHAPTER 5

Conclusions and Recommendations

5.1 Conclusions

5.1.1 TDO characterisation

TDO was characterised for chemical composition using a GC-FID. The target compounds, limonene and benzothiazole, were detected in the TDO. Limonene-like impurities such as p-cymene and trimethylbenzene were also detected. The concentration of limonene in this study's TDO is low compared to limonene concentrations in literature. An acceptable explanation for the low limonene concentration is the range of pyrolysis parameters applied.

Total sulphur (5300 ppm) in this study's TDO is also low compared to other studies in literature. In this study, chemical composition analysis showed that benzothiazole accounts for 60% of the total sulphur. The concentration of benzothiazole is also comparable to benzothiazole concentrations in literature. The species concentration was estimated with an average error of 7.45%. The low sulphur content of this study's TDO is also due to pyrolysis parameter range. For fuel use, SANS specifies a sulphur concentration of less than 500 ppm. Besides total sulphur and flash point, the fuel properties of this study's TDO are close to fuel properties specified by SANS 342.

5.1.2 OSN separation performance

It was found that the PM-280 and ST-228 membrane allow permeation of pure species. The pure species flux through PM-280 at 30 bar ranged from 75 to 297 L.m⁻².h⁻¹. The pure species flux through ST-228 at 30 bar ranged from 48 to 93 L.m⁻².h⁻¹. The permeation of limonene and limonene-like impurities was comparable through both membranes. The flux of p-cymene and 1,2,4-trimethylbenzene through PM-280 was 1.88 and 1.44 times faster than that of limonene respectively. It was found that pure species fail to permeate through DM-200. Pure benzothiazole demonstrated a destructive nature on the surface of PM-280 and ST-228 membrane.

The flux of a species was found to be directly proportional to the transmembrane pressure.

The parameters that influenced the permeation of pure species through OSN membranes were found to be species-membrane interaction properties (mutual affinity), viscosity and species structural properties such as size and geometry. The relationship between the flux and these parameters was found to be described by Equation 4.4.

$$Flux \propto \left(\frac{molecular\ size}{1}\right) \times \left(\frac{1}{viscosity}\right) \times \left(\frac{1}{affinity}\right) \quad (4.4)$$

Concerning the purification of TDO through OSN membranes, it was found that:

- The flux of crude TDO (0.877 L.m⁻².h⁻¹) through PM-280 decreases gradually with time to a point of zero permeation due to concentration polarization.

- Crude TDO fails to permeate through ST-228 and DM-200.
- Limonene, benzothiazole and other species from crude TDO achieve negative rejections through PM-280. A negative rejection is a positive result for limonene purification since it implies that a proportion of limonene is being recovered on the permeate side. Purification of crude TDO by PM-280 produced a 5% limonene recovery.

In terms of diluting the TDO as a plan of improving the TDO flux and purification of TDO components, it was found that:

- Dilution increases TDO flux. TDO diluted with toluene (1:1) permeates through ST-228 at $7.5 \text{ L.m}^{-2}.\text{h}^{-1}$. The flux of the diluted TDO depends on the solvent used for dilution.
- Dilution improves species recovery (produces much lower negative rejections). Purification of diluted TDO produced a 15% limonene recovery. Overall benzothiazole reduction was 6.3%.
- The transport of species in diluted TDO is influenced by species-membrane interactions (solubility parameter difference). A strong mutual affinity between the species and the membrane surface results in low or even negative rejection.

In terms of studying the effect of species concentration on membrane rejection performance, it was found that:

- Species concentration has no effect on membrane rejection performance.

5.1.3 Comparison between TDO purification by OSN and traditional techniques

In terms of limonene recovery, it was found in literature (Stanciulescu and Ikura, 2006) that a single stage distillation process recovers much more than OSN. While OSN recovers 5% from crude TDO, distillation recovers approximately 32-37 wt%. The limonene recovery through OSN goes up to 15% using pre-treated TDO. However, the purification of TDO through OSN is achieved using much less energy compared to distillation.

In terms of sulphur reduction, it was found that OSN compares well with catalytic reactions during pyrolysis. OSN was found to reduce 6.3% of benzothiazole in TDO while catalytic reactions reduce 5.0% of sulphur in TDO. Gas-phase desulphurization distillation has achieved much more than any other technique. It was found that distillation can reduce up to 90.3% of total sulphur in TDO. No technique in relevant literature has met the TDO sulphur concentrations specified by SANS 342.

5.2 Recommendations

This work demonstrated that it is possible to purify TDO through OSN membranes but not at the level of distillation. From the findings of this study, recommendations for future work are:

- **Pre-treatment of TDO**

Distillation can be used as a pre-treatment technique to fractionate TDO. Heating the oil at approximately 150°C-200°C will separate the oil into a light fraction and a heavy fraction. Heating the heavy fraction at approximately 185°C will then separate the middle fraction that contains limonene from the heavy fraction. Studies (Ngwetjana, 2015; Stanciulescu and Ikura, 2006) show that the limonene enriched fraction that is obtained after heating the heavy fraction contains traces of light compounds such as toluene and ethylbenzene.

A non-polar OSN membrane that holds a MWCO of between 150-200 g/mol can be used to increase the limonene concentration from the reported 32-37 wt% (Ngwetjana, 2015; Stanciulescu and Ikura, 2006) to concentrations greater than 50 wt%. Limonene concentration increment will be due to the permeation of light compounds and the retention of limonene by the membrane.

- **Multi-stage OSN separation**

Hydrophobic OSN membranes having MWCO's ranging from 500 to 350 g/mol can be used to fractionate the oil. This will reduce concentration polarization when using membranes such as PM-280 and ST-228.

5.3 References

Ngwetjana, M.M., 2017. Fractionation of tyre derived oil (TDO).

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APPENDIX A

Detailed Experimental Procedures

A.1 Step by step procedures for OSN experiments

A.1.1 Membrane pretreatment and steady-state characterisation

1. Load membrane cell with 250 ml toluene.
2. Fasten bolts of the membrane's cell top flange.
3. Place membrane cell on a magnetic stirrer and set stirrer speed to 500 rpm.
4. Place a 100 ml collection flask close to the membrane cell so that the permeate flows from the cell's outlet pipe into the collection flask.
5. Connect the nitrogen cylinder gas line to the membrane cell gas inlet.
6. Set the pressure in the membrane cell to 30 bar
7. Allow 50 ml of the feed to permeate into the collection flask. Discard the permeate in the collection flask. The permeate should be yellowish in colour due to the preservation oil.
8. Depressurise the cell, open the membrane cell and add 50 ml of fresh toluene.
9. Close the membrane cell and pressurise at 30 bar.
10. Allow 150 ml of toluene to permeate.
11. During permeation, measure the flux as volume of permeate collected per unit time and surface area. If a steady flux is achieved by the membrane, the pretreatment step is complete. If steady state flux is not achieved, repeat steps 7-11.

A.1.2 TDO purification

1. Load the membrane cell with 150 ml TDO.
2. Secure the top flange of the membrane cell by fastening bolts.
3. Place the membrane cell on top of a magnetic stirrer and set stirrer speed to 500 rpm.
4. Direct the permeate pipe from the cell to a 100 ml collection flask.
5. Connect the Nitrogen cylinder gas line to the cell's gas inlet.
6. Set the pressure in the membrane cell to 30 bar.
7. Allow TDO to permeate.
8. During permeation, measure the flux as volume of permeate collected per unit time and surface area. If steady state flux is achieved, depressurise cell, open cell and permeate back into the cell. If steady flux is not achieved, repeat steps 2-8.
9. After attaining steady flux and returning the permeate into the cell, pressurise the cell at 30 bar and allow TDO to permeate.
10. Take a sample (1×5ml) of the permeate.
11. Depressurise and open the membrane cell.
12. Take a sample (1×5ml) of the retentate.
13. Analyse samples with GC.

APPENDIX B

Raw Experimental Data

B.1 Pure species Flux**Table B.1:** Toluene dynamics and steady-state flux data at 30 bar

Membrane PM-280 Conditions 30 bar, 22°C, 500 rpm					
Volume (ml)	Raw data			Calculated data	
	ΔV (ml)	Time (min)	Δt (min)	Dynamic flux ($L.m^{-2}.h^{-1}$)	Steady-state flux ($L.m^{-2}.h^{-1}$)
10	10	1	1	377.35	
20	10	2.27	1.27	297.13	
30	10	3.54	1.26	297.65	297.65
40	10	4.81	1.26	297.82	297.82
50	10	6.08	1.27	297.36	297.36
60	10	7.35	1.27	297.65	297.65
70	10	8.62	1.27	297.88	297.88

Table B.2: Limonene dynamics and steady-state flux data at 30 bar

Membrane PM-280 Conditions 30 bar, 22°C, 500 rpm					
Volume (ml)	Raw data			Calculated data	
	ΔV (ml)	Time (min)	Δt (min)	Dynamic flux ($L.m^{-2}.h^{-1}$)	Steady-state flux ($L.m^{-2}.h^{-1}$)
10	10	4	4	94.34	
20	10	8.5	4.5	83.86	
30	10	13	4.5	83.86	83.86
40	10	18	5	75.47	
50	10	23	5	75.47	75.47
60	10	28	5	75.47	75.47
70	10	33	5	75.47	75.47

Table B.3: 1,2,4-Trimethylbenzene dynamics and steady-state flux data at 30 bar

Membrane PM-280 Conditions 30 bar, 22°C, 500 rpm					
Volume (ml)	Raw data			Calculated data	
	ΔV (ml)	Time (min)	Δt (min)	Dynamic flux ($L.m^{-2}.h^{-1}$)	Steady-state flux ($L.m^{-2}.h^{-1}$)
10	10	2.5	2.5	150.94	
20	10	5	2.5	150.94	150.94
30	10	8.6	3.6	104.82	
40	10	12.2	3.6	104.82	104.82
50	10	15.8	3.6	104.82	104.82
60	10	19.4	3.6	104.82	104.82
70	10	23	3.6	104.82	104.82

Table B.4: p-Cymene dynamics and steady-state flux data at 30 bar

Membrane PM-280 Conditions 30 bar, 22°C, 500 rpm					
Volume (ml)	Raw data			Calculated data	
	ΔV (ml)	Time (min)	Δt (min)	Dynamic flux ($L.m^{-2}.h^{-1}$)	Steady-state flux ($L.m^{-2}.h^{-1}$)
10	10	2	2	188.68	
20	10	4.75	2.75	137.22	
30	10	7.5	2.75	137.22	137.22
40	10	10.3	2.78	135.74	
50	10	13.0	2.75	137.22	
60	10	15.8	2.75	137.22	137.22
70	10	18.5	2.75	137.22	137.22

B.2 Pure species permeance**Table B.5: Pure species permeance**

Membrane PM-280 Conditions 19°C, 500 rpm				
	10 bar	20 bar	30 bar	40 bar
<i>Permeance $L.m^{-2}.h^{-1}.bar^{-1}$</i>				
Limonene	2.3	2.7	2.5	2.3
p-cymene	4.7	4.6	4.6	4.2
1,2,4-Trimethylbenzene	3.4	3.6	3.5	3.0
Toluene	9.5	9.5	9.9	9.3
Benzothiazole	-	-	-	-

Table B.6: Pure species permeance

Membrane ST-228 Conditions 19°C, 500 rpm				
	10 bar	20 bar	30 bar	40 bar
<i>Permeance $L.m^{-2}.h^{-1}.bar^{-1}$</i>				
Limonene	1.6	1.8	1.6	1.4
p-cymene	1.6	1.4	1.4	1.4
1,2,4-Trimethylbenzene	1.0	1.0	1.2	1.0
Toluene	3.1	3.1	3.1	3.3
Benzothiazole	-	-	-	-

B.3 TDO Flux**Table B.7:** TDO dynamics and steady-state flux data at 30 bar

Membrane PM-280 Conditions 30 bar, 22°C, 500 rpm					
Volume (ml)	Raw data			Calculated data	
	ΔV (ml)	Time (min)	Δt (min)	Dynamic flux ($L.m^{-2}.h^{-1}$)	Steady-state flux ($L.m^{-2}.h^{-1}$)
1	1	30	30	1.26	
2	1	58	28	1.35	
3	1	101	43	0.88	
4	1	144	43	0.88	0.877
5	1	200	56	0.67	
6	1	262	62	0.61	
7	1	322	60	0.63	

Table B.8: TDO/Toluene dynamics and steady-state flux data at 30 bar

Membrane PM-280 Conditions 30 bar, 22°C, 500 rpm					
Volume (ml)	Raw data			Calculated data	
	ΔV (ml)	Time (min)	Δt (min)	Dynamic flux ($L.m^{-2}.h^{-1}$)	Steady-state flux ($L.m^{-2}.h^{-1}$)
2	2	3	3	25.16	
4	2	7	4	18.77	
6	2	11	4	18.77	
8	2	16	5	15.10	
10	2	21	5	15.10	15.10
12	2	26	5	15.10	15.10
14	2	31	5	15.10	15.10
16	2	36	5	15.10	15.10
18	2	41	5	15.10	15.10
20	2	46	5	15.10	15.10
22	2	51	5	15.10	15.10

Table B.9: TDO/Toluene dynamics and steady-state flux data at 30 bar

Membrane ST-228 Conditions 30 bar, 22°C, 500 rpm					
Volume (ml)	Raw data			Calculated data	
	ΔV (ml)	Time (min)	Δt (min)	Dynamic flux ($L.m^{-2}.h^{-1}$)	Steady-state flux ($L.m^{-2}.h^{-1}$)
2	2				
4	2	11	11	6.87	
6	2	22	11	6.87	6.87
8	2	33	11	6.87	6.87
10	2	45	12	6.29	
12	2	57	13	5.79	
14	2	70	13	5.79	5.98
16	2	83	14	5.39	

B.4 Species recovery data**Table B.10: species recovery data after TDO purification by OSN**

Membrane PM-280 Conditions 30 bar, 20°C, 500 rpm				
Species	Feed (ppm)	Permeate (ppm)	Retentate (ppm)	Rejection (%)
Limonene	15,106.7	16,169.9	11,554.4	-7
Benzothiazole	3126.1	3314.4	2441.5	-6
p-cymene	5957.4	6610.4	5255.8	-11
1,2,4-trimethylbenzene	650.4	664.5	642.3	-2
Toluene	1544.9	1774.9	1654.1	-15

Table B.11: Species recovery after TDO/toluene purification by OSN

Membrane ST-228 Conditions 30 bar, 21°C, 500 rpm				
Species	Feed (ppm)	Permeate (ppm)	Retentate (ppm)	Rejection (%)
Limonene	3271.1	3606.5	3278.4	-10
1,2,4-Trimethylbenzene	677.4	1113.1	796.9	-64
p-Cymene	6353.4	7762.8	6665.9	-22
Benzothiazole	1797.2	3566.4	1683.2	-98
2-Ethyltoluene	308.4	442.3	368.2	-43
Toluene	349133.6	447249.4	350645.4	-28

Table B.12: Species recovery after TDO/1-octene purification by OSN

Membrane ST-228 Conditions 30 bar, 19°C, 500 rpm				
Species	Feed (ppm)	Permeate (ppm)	Retentate (ppm)	Rejection (%)
Limonene	2821.6	2292.5	3130.5	18.8
Benzothiazole	1274.4	1148.8	1425.5	9.9
p-Cymene	4880.8	4118.8	5443.6	15.6
1,2,4-Trimethylbenznene	567.8	501.4	663.5	11.8

Table B.13: Species recovery after TDO/Ethanol purification by OSN

Membrane ST-228 Conditions 30 bar, 19°C, 500 rpm				
Species	Feed (ppm)	Permeate (ppm)	Retentate (ppm)	Rejection (%)
Limonene	2944.4	2835.5	3144.3	3.7
Benzothiazole	1436.3	1396.9	1482.6	2.8
p-Cymene	5127.9	4961.2	5483	3.3
1,2,4-Trimethylbenznene	623.1	590.5	662.3	5.2

Table B.14: Concentration varying experiment

Membrane ST-228 Conditions 21°C, 500 rpm	Concentration (ppm)				
	50000	75000	100000	125000	150000
<i>Rejection (%)</i>					
Limonene	15	-0.6	-2.3	-0.3	14
p-cymene	9.1	-2.8	15	-4	13
1,2,4-Trimethylbenzene	18.8	-4	14.9	-6	13
Toluene	-192	-197	-178	-202	-183
Benzothiazole	2.3	-9	13	-10	6.4

APPENDIX C

Sample Calculations

C.1 Permeate flux

The active membrane area (A) is used for calculating the flux (J) of the feed through the membrane. It can be estimated by measuring the inner diameter of the membrane cell.

Inner diameter of membrane cell is 45 mm.

$$A = \pi r^2 = \pi (22.5\text{mm})^2 = 1590.43\text{mm}^2 = 0.00159\text{m}^2$$

The volume and time differences (Δv and Δt respectively) are used to calculate the dynamic volume flux of TDO at 30 bar.

$$J_V = \frac{0.001\text{ L}}{0.00159\text{m}^2 \times 0.9\text{ h}} = 0.698\text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$$

$$J_V = \frac{0.001\text{ L}}{0.00159\text{m}^2 \times 1.15\text{ h}} = 0.547\text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$$

Steady-state volume flux is only recorded when dynamic flux is observed to remain constant.

C.2 Species recovery

The species concentration in the feed and permeate solutions was measured using a GC-FID.

Limonene concentration in feed: 15,106.7 ppm

Limonene concentration in permeate: 16,169.9 ppm

$$R = \left(1 - \frac{c_p}{c_f}\right) \times 100\%$$

$$\therefore R = \left(1 - \frac{16,169.9\text{ ppm}}{15,106.7\text{ ppm}}\right) \times 100\% = -7.03\%$$

C.3 Solubility parameter

Figure C.1 presents the molecular structures of organic compounds discussed in this study.

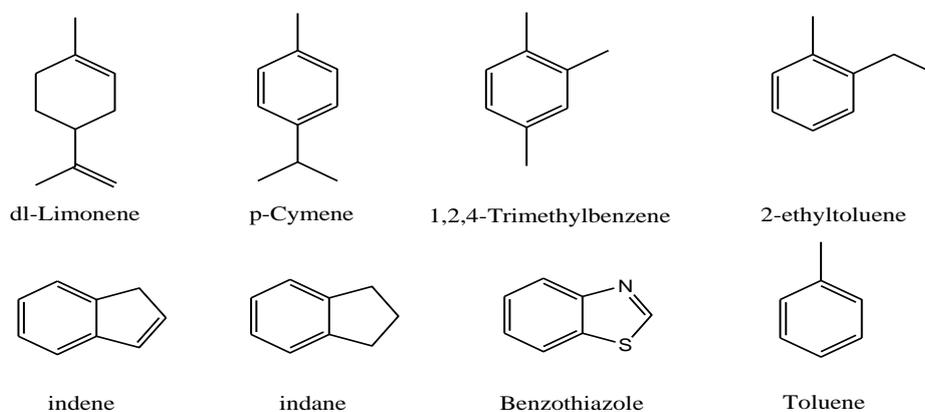


Figure C.1: Molecular structures of compounds discussed in this study.

As described by Fedors (Fedors, 1973), the solubility parameter (δ) of a specific liquid is conveniently estimated by using equation C.1.

$$\delta = \sqrt{\frac{\Delta E_V}{V_m}} \quad (C.1)$$

ΔE_V is the energy of vaporization at a given temperature

V_m is the molar volume

This method of calculating solubility parameters is based on the addition of functional group constants (group additive method) and is widely accepted in literature (Fedors, 1973; Hansen, 2007; Van Krevelen, 2009) as a convenient way of estimating δ .

Table 1 presents the E_V and V_m functional group constants that were used to estimate the solubility parameters of organic compounds in this study. The energy of vaporization constants were measured at 25 °C.

Table C.1: Functional group contributions to E_V and V_m at 25 °C (adapted from Fedors, 1973).

Functional group or atom	E_V (Cal/mol)	V_m (cm ³ /mol)
CH ₃	1125	33.5
CH ₂	1180	16.1
CH	820	-1.0
C	350	-19.2
H ₂ C=	1030	28.5
-CH=	1030	13.5
=C=	1030	-5.5
HC≡	920	27.4
5/more membered ring	250	16
3 or 4 membered ring	750	18
Conjugated double bonds in ring	400	-2.2
Halogen attached to C=	-20% of E_V of halogen	4.0
N	1000	-9.0
NH	2000	4.5
NH ₂	3000	19.2
-N=	2800	5.0
S	3380	12

Equation C.1 was used to calculate the solubility parameters of compounds listed in Table C.2.

Table C.2: Solubility parameters of compounds discussed in this project

Compound	ΣE_V (Cal/mol)	ΣV_m (cm ³ /mol)	δ (MPa ^{0.5})
Limonene	11130	163.9	16.4
P-Cymene	11825	156.3	17.4
1,2,4-Trimethylbenzene	11005	133.9	18.2
Indane	11120	111.5	19.8
Benzothiazole	14530	98.9	24.2
2-Ethyltoluene	11060	135.5	18.0
Toluene	8755	109.3	17.8

The solubility parameter difference is a general description of the mutual affinity between solvents, non-solvents and polymers. A small solubility parameter difference indicates high affinity and better miscibility. The mutual affinities between the components in TDO and the polymer material of the membrane are presented in table B.3. The puramem and duramem membranes are fabricated by the P84 lenzing polyimide polymer which has a Hansen solubility parameter of 27.1 MPa^{0.5}

Table C.3: Solubility parameter differences between TDO components and P84 polymer.

TDO component	$(\delta_{P84-component})(\text{MPa}^{0.5})$
Limonene	10.7
P-cymene	9.6
1,2,4-Trimethylbenzene	8.8
Indene	7.2
Benzothiazole	2.8
2-Ethyltoluene	9.0
Toluene	9.2

C.4 Limonene overall recovery and benzothiazole reduction

Limonene overall recovery after purification was calculated by comparing the feed and permeate concentrations.

Limonene concentration in feed: 3271.1 ppm

Limonene concentration in permeate: 3606.5 ppm

$$3271.1 \frac{\text{mg}}{\text{L}} \times 0.15 \text{ L} = 490.67 \text{ g}$$

$$3606.5 \frac{\text{mg}}{\text{L}} \times 0.02 \text{ L} = 72.13 \text{ g}$$

$$\therefore \text{overall recovery} = \frac{72.13 \text{ g}}{490.67 \text{ g}} \times 100\% = 14.7\%$$

Benzothiazole reduction from crude TDO was estimated by comparing benzothiazole concentration in the feed and retentate solutions.

Benzothiazole concentration in feed: 1797.2 ppm

Benzothiazole concentration in retentate: 1683.2 ppm

$$\text{Benzothiazole reduction} = \frac{\text{concentration in feed} - \text{concentration in retentate}}{\text{concentration in feed}}$$

$$\therefore \text{Benzothiazole reduction} = \frac{1797.2 - 1683.2}{1797.2} \times 100\% = 6.3\%$$

APPENDIX D

Analytical procedures and calibrations

D.1 Preparing standards and samples

1. Prepare standards (25000 ppm) using the pure analytical chemicals and DCM as a solvent.
2. From the standards prepared, prepare a cocktail of standards (2500 ppm) by simply adding 1000 μL of each standard in a 10000 μL vial.
3. Add 40 μL of already prepared 5000 ppm internal standards solution into the cocktail solution.
4. From the cocktail solution, prepare six standards of 3.16 ppm; 7.81 ppm; 15.6 ppm; 30.15 ppm; 62.15 ppm and 125 ppm.
5. Prepare GC samples from the six standards prepared and analyse.

GC calibration curves are presented in figures D.1 to D.7

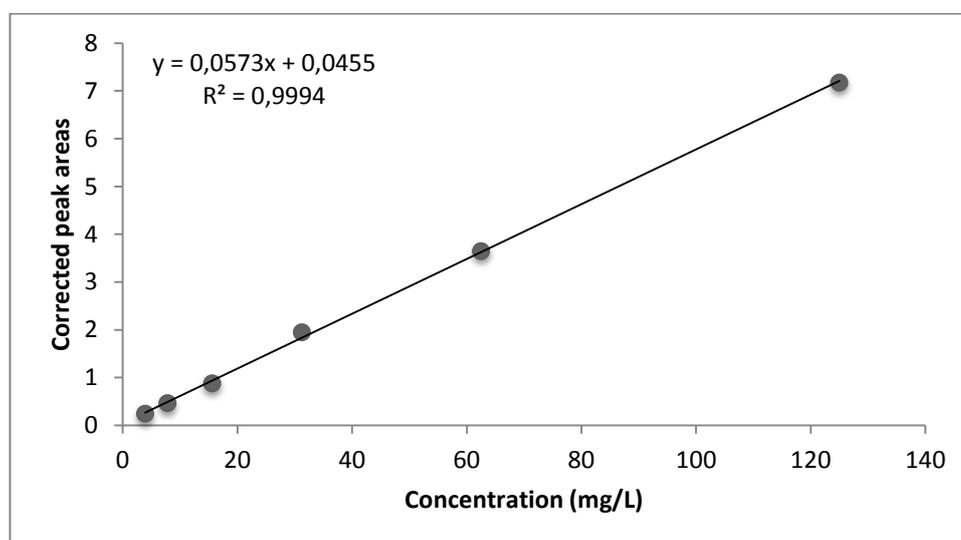


Figure D.1: dl-Limonene calibration curve.

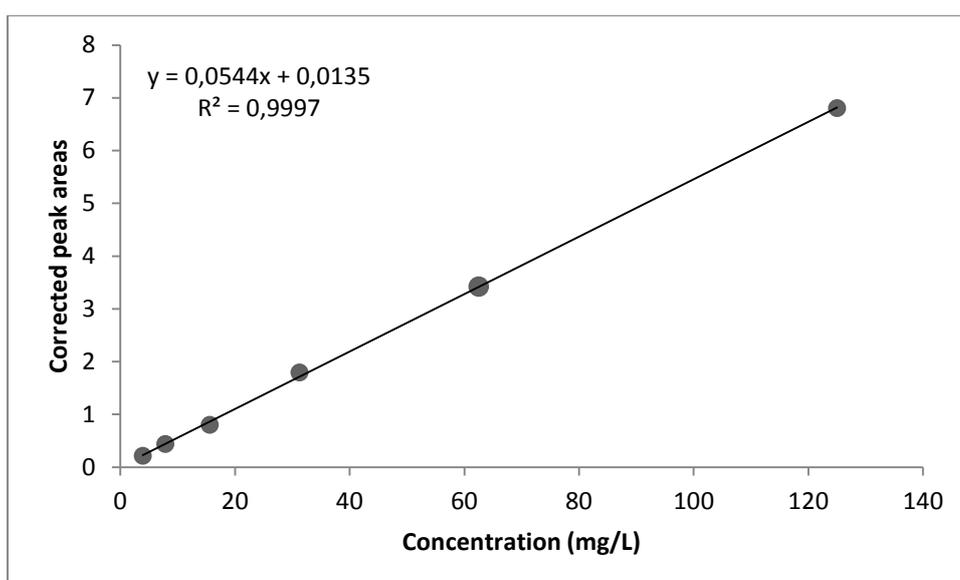


Figure D.2: 1,2,4-Trimethylbenzene calibration curve.

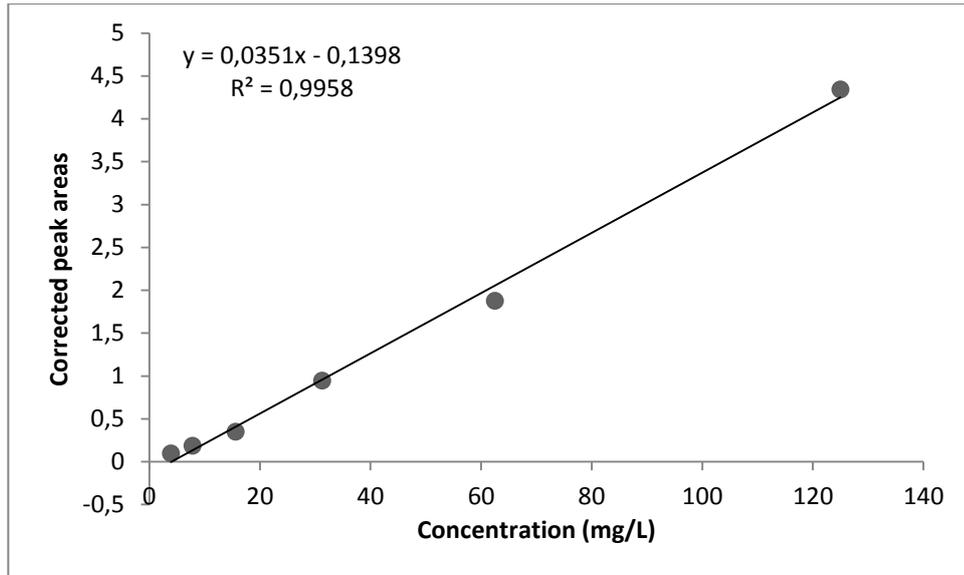


Figure D.3: Benzothiazole calibration curve.

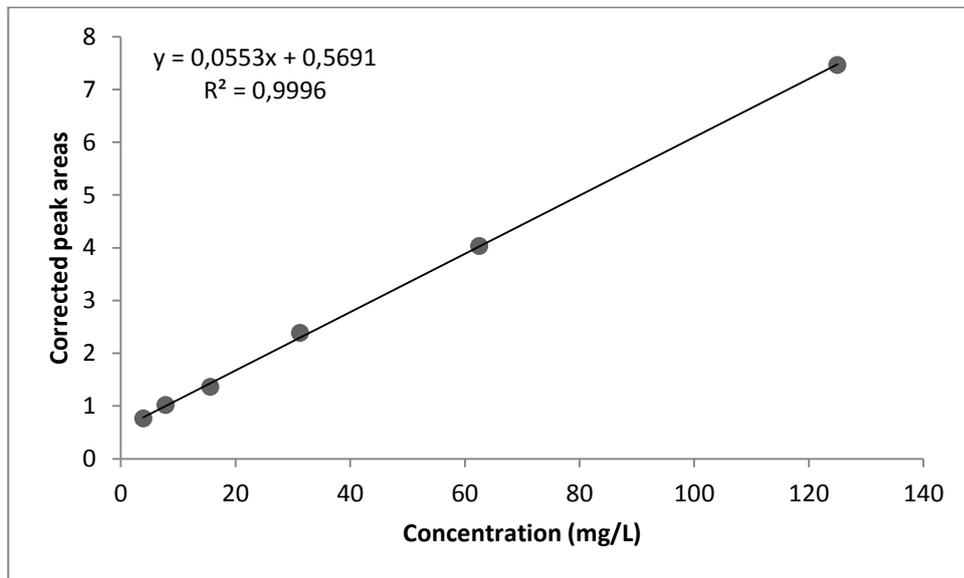


Figure D.4: Toluene calibration curve.

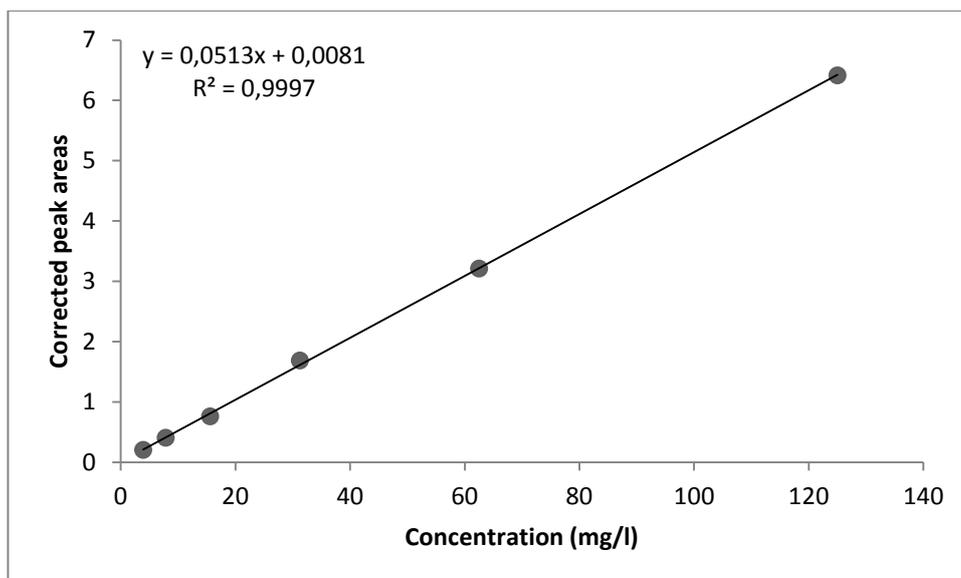


Figure D.5: 2-Ethyltoluene calibration curve.

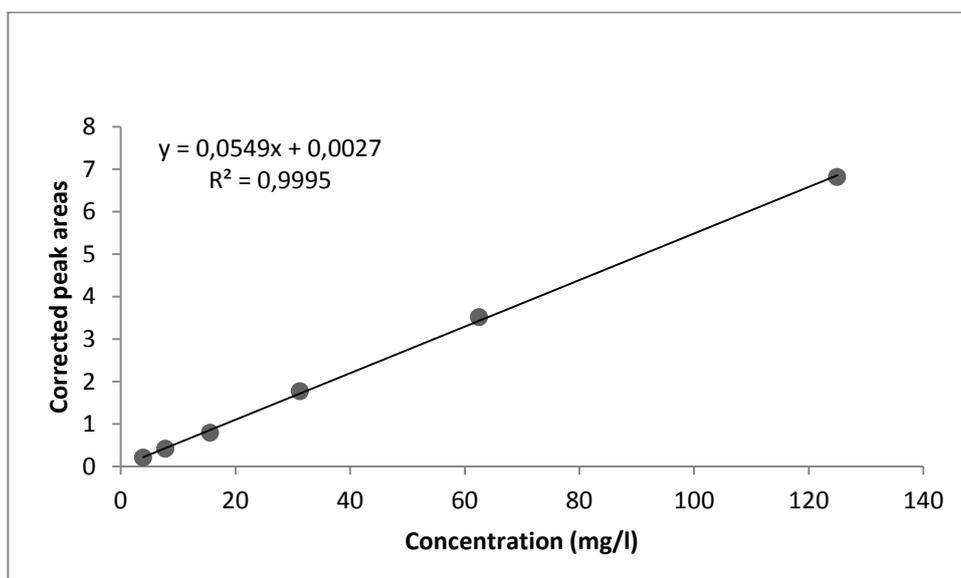


Figure D.6: indene calibration curve.

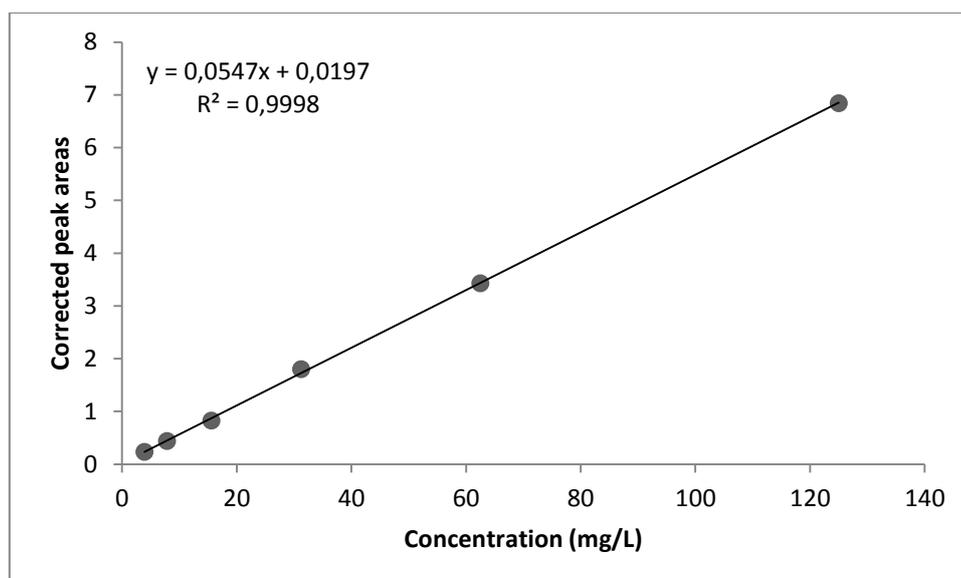


Figure D.7: P-cymene calibration curve.

D.2: GC raw experimental data**Table D.1:** GC raw data after TDO/toluene purification by STTM-228

	Feed	Permeate Solute peak areas	Retentate
Limonene	36.09508	42.45250	32.43343
p-Cymene	76.68430	91.81298	68.55284
1,2,4-Trimethylbenzene	8.37891	13.32661	8.36837
Benzothiazole	9.61816	21.13531	8.02099
Toluene	4246.54932	5334.95801	3636.98120
2-Ethyltoluene	3.64800	5.05821	3.68603
Toluene-d8	21.93028	21.52075	18.70139
Napthalene-d8	19.57526	19.00688	17.79991
α -pinene	18.80092	20.09900	16.85400
	Solute peak area/ISTD peak area		
Limonene	1.91986	2.1122	1.9244
p-Cymene	3.4967	4.2663	3.6656
1,2,4-Trimethylbenzene	0.3821	0.6192	0.4475
Benzothiazole	0.4913	1.1119	0.4506
Toluene	193.6386	247.8983	194.4765
2-Ethyltoluene	0.1663	0.2350	0.1971

Table D.2: GC raw data after TDO/1-octene purification by STTM-228

	Feed	Permeate	Retentate
	Solute peak areas		
Limonene	31.61827	23.71330	31.00409
p-Cymene	60.58348	46.80962	59.74643
1,2,4-Trimethylbenzene	7.26137	5.89577	7.46349
Benzothiazole	6.21461	5.14182	6.94504
Toluene	31.23235	73.67468	33.60383
2-Ethyltoluene	1.51028	1.51169	1.32531
Toluene-d8	22.52621	20.59685	19.93254
Napthalene-d8	20.20781	19.51745	19.26266
α -pinene	19.02130	17.44761	16.85648
	Solute peak area/ISTD peak area		
Limonene	1.662256	1.359115	1.839298
p-Cymene	2.689466	2.272659	2.997432
1,2,4-Trimethylbenzene	0.322352	0.286246	0.374437
Benzothiazole	0.307535	0.263447	0.360544
Toluene	1.386489	3.576988	1.685878
2-Ethyltoluene	0.067045	0.073394	0.06649

Table D.3: GC raw data after TDO/ethanol purification by STTM-228

	Feed	Permeate	Retentate
	Solute peak areas		
Limonene	27.92664	28.30473	28.30473
p-Cymene	54.99083	54.94581	54.94581
1,2,4-Trimethylbenzene	6.86149	6.72855	6.72855
Benzothiazole	6.67522	6.70149	6.70149
Toluene	28.84862	21.36318	21.36318
2-Ethyltoluene	1.59990	1.61695	1.61695
Toluene-d8	19.46780	20.10113	20.10113
Napthalene-d8	18.32098	19.11926	19.11926
α -pinene	16.11817	16.94664	16.94664
	Solute peak area/ISTD peak area		
Limonene	1.73261853	1.670227	1.670227
p-Cymene	2.82470695	2.733469	2.733469
1,2,4-Trimethylbenzene	0.35245328	0.334735	0.334735
Benzothiazole	0.36434841	0.35051	0.35051
Toluene	1.48186338	1.062785	1.062785
2-Ethyltoluene	0.08218186	0.080441	0.080441