



Chemical recycling of polyethylene and polypropylene by catalysed dehydrogenation and metathesis

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PREFACE

Declaration of authorship

I, Daniël Jacobus (Jaco) Becker, hereby declare that the dissertation entitled: **Chemical recycling of polyethylene and polypropylene by catalysed dehydrogenation and metathesis**, which I herewith submit to the North-West University is in compliance with the requirements set for the degree: Master's in Chemical Engineering, is my own work, has been text-edited in accordance with the requirements and has not already been submitted to any other university.

DJ Becker

Signed on the 27th day of November 2025

Conference presentations and articles

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ABSTRACT

Polyethylene (PE) and polypropylene (PP) constitute the largest fraction of global plastic waste and pose significant challenges for conventional chemical and mechanical recycling routes due to chemical inertness and mechanical downcycling. This study explores a novel chemical recycling pathway using tandem dehydrogenation and olefin cross-metathesis (TDOCM) to degrade virgin, recycled and consumer grade PE and PP under mild conditions (300 °C), producing exclusively linear alkane products in 3 hours. The process employs a fully heterogeneous catalyst system consisting of Pd/ γ -Al₂O₃ for dehydrogenation and WO_x/SiO₂ for metathesis, with n-decane as the light alkane co-reagent. It is also the first time that the degradation of PP using this reaction pathway has been reported.

Initial validation experiments confirmed complete degradation of virgin HDPE, LDPE, and PP at 300 °C and moderate pressures, with both yielding exclusively alkane products and no detectable aromatics or olefins. For PE samples, including commercial-grade feedstocks with additives, the system exhibited consistent performance and high conversion (up to 80 wt.% liquid yields). PP, despite its branched and tertiary carbon structure, underwent rapid breakdown with >80 wt.% oil yields and showed enhanced iso-alkane selectivity compared to PE products, due to retained methyl side chains post-metathesis.

Parametric studies revealed that product distributions are sensitive to polymer type, reaction time, catalyst loading, alkane-to-polymer ratios, and pressure. For PE, insufficient light alkane presence led to increased wax and gas yields due to redundant metathesis reactions, while for PP, lower alkane concentrations favoured β -scission over the TDOCM route, increasing gaseous by-products. Elevated pressures improved alkane incorporation across both polymer types by enhancing hydrogen solubility and stabilising reactive intermediates. Lastly, petroleum ether was evaluated as a cost-effective substitute for n-decane. Despite its branched profile, it supported effective polymer breakdown with exclusively alkane products and offered advantages in ease of post-reaction separation.

This work demonstrates the viability of TDOCM as a mild and selective method for PE and PP recycling, with the ability to tune product profiles and optimise reaction economics through thoughtful selection of conditions and reagents. It addresses the shortcomings of mechanical recycling and conventional chemical recycling alternatives by offering mild operating conditions and a narrow product spectrum suitable for downstream upgrading.

Keywords: *polyethylene, polypropylene, chemical recycling, dehydrogenation, metathesis, tandem heterogeneous catalysis*

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ABBREVIATIONS

Abbreviation or acronym	Description
Afrox	African oxygen
ASTM	American Society for Testing and Materials
ATR-FTIR	Attenuated total reflection Fourier-transform infrared
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
DCM	Dichloromethane
DSC	Differential Scanning Calorimetry
EDS	Energy-dispersive X-ray spectroscopy
FID	Flame Ionization Detector
FTIR	Fourier-transform infrared spectroscopy
GC	Gas chromatography
GC-MS	Gas chromatography-mass spectrometry
PDI	Polydispersity index
PE	Polyethylene
PP	Polypropylene
SEM	Scanning electron microscope
TCD	Thermal conductivity detector
TDOCM	Tandem dehydrogenation and olefin cross metathesis
wt. %	Weight Percentage
XRD	X-ray diffraction
XRF	X-ray fluorescence

NOMENCLATURE

Symbol	Unit	Description
m_i	g	Mass of component i
M_n	g/mol	Number average molecular weight
MW_i	g/mol	Molecular weight of component i
n_i	Mol	Mol amount of component i
P	atm	Pressure
R	L·atm/mol·K	Universal gas constant
T	K	Temperature
V	dm ³	Volume
x_i	-	Mol fraction of component i

CHAPTER 1 INTRODUCTION

1.1 Background and motivation

Plastics are lightweight, durable, versatile, and relatively inexpensive to manufacture, making them integral to various industries such as electronics, automotive, and healthcare (Gopinath et al., 2020). As a result, global plastic production exceeds 300 million tons annually and is projected to reach 500 million tons by 2025 (Zhang et al., 2021). This trend is also observed in South Africa, where plastic production increased from 1.8 million tons in 2015 to 2.7 million tons in 2017 (Williams-Wynn and Naidoo, 2020). Only 70% of the waste generated in South Africa is collected (Olatayo et al., 2021). Of this collected waste, 14% is mechanically recycled, 45% is disposed of in sanitary landfills or incineration facilities, and the remaining 11% is disposed of in unsanitary landfills (IUCN-EA-QUANTIS, 2020).

Due to increasingly strict legislation and adverse environmental impacts, disposing of plastic waste in landfills is becoming less desirable (Achilias, 2007). Similarly, incineration is becoming a less common waste management technique due to the release of greenhouse gases. Additionally, polymeric materials are produced from oil and gas, resources that are becoming increasingly scarce (Datta and Kopczyńska, 2016). Thus, to conserve sparse natural resources and limit environmental pollution, there has been an increase in the amount of plastic waste subjected to mechanical recycling (Hamad et al., 2013). Mechanical recycling involves separating the polymer from its associated contaminants and reprocessing it via hot melt extrusion (Hamad et al., 2013).

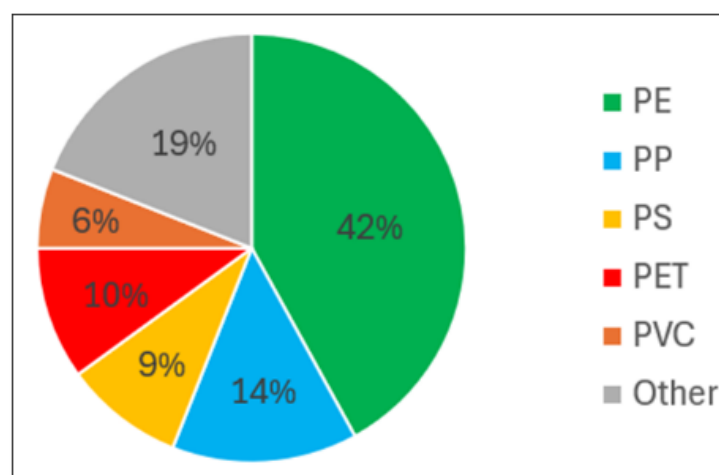


Figure 1-1: Average composition of plastic waste streams (Bodzay and Bánhegyi, 2016)

However, as seen in Figure 1-1, plastic waste streams consist mostly of polyethylene (PE) and polypropylene (PP). When subjected to mechanical recycling, these polymers are downgraded such that they are unusable after a few cycles (Esmizadeh et al., 2019).

To address the shortcomings of landfilling, incineration, and mechanical recycling, researchers have explored the field of chemical recycling of polymers as a potential alternative waste management strategy (Miao et al., 2021). The most prominent chemical recycling methods are pyrolysis, solvolysis, and hydrocracking. These methods can be used to successfully degrade PP and PE to valuable waxes and liquids, which can be converted into fuels or lubricants, among other valuable products (Thiounn and Smith, 2020). However, pyrolysis reactions generally occur at elevated temperatures ranging from 600–800 °C, and solvolysis and hydrocracking reactions require expensive solvents or hydrogen-rich atmospheres. Furthermore, all these methods produce a complex distribution of products ranging from olefins, alkanes, and aromatic compounds, which require extensive separation steps before they can be utilised (Thiounn and Smith, 2020). Resultantly, pyrolysis, solvolysis, and hydrocracking have limited industrial applications due to a lack of economic viability.

Recent studies by Jia et al. (2016), Ellis et al. (2021), and Kim et al. (2022) demonstrated that polyethylene (PE) feedstocks can be degraded into a mixture of alkane products through a tandem catalytic strategy involving dehydrogenation followed by olefin cross-metathesis. This strategy offers potential for industrial application in the recycling of polyethylene (PE) and polypropylene (PP), as it proceeds under relatively mild conditions, employs inexpensive alkanes as co-feedstocks, operates in an inert atmosphere, and selectively yields alkanes as the sole products (Ellis et al., 2021).

1.2 Problem statement

Landfilling, incineration, and mechanical recycling of polyethylene and polypropylene are unsustainable waste management strategies. Additionally, current chemical recycling strategies for these polymers operate under harsh conditions, utilise expensive solvents, require extensive feedstock sorting, and deliver a complex distribution of products. The development of a tandem heterogeneously catalysed dehydrogenation and olefin cross-metathesis process to depolymerise PE and PP to a mixture of alkane products, using inexpensive alkane solvents at mild reaction conditions, would address these concerns.

1.3 Aim and objectives

1.3.1 Aim

Demonstrate that Pd/ γ -Al₂O₃ and WO_x/SiO₂ can successfully degrade PE and PP via tandem dehydrogenation and olefin cross-metathesis under mild reaction conditions to produce only alkanes as products and to investigate how different reaction parameters influence the system.

1.3.2 Objectives

To achieve the aim of this study, the following objectives were formulated:

- Characterise the polymer feedstocks and the catalysts using advanced analytical techniques.
- Test the efficiency of the catalyst system in degrading polymer samples.
- Investigate the applicability of the catalyst system on other polymer grades and types.
- Characterise the gases, oils, and solid residues produced from the experiments using advanced analytical techniques.
- Identify and evaluate the predominant factors influencing the yield and composition of products.

1.4 Scope

Various types and grades of polyethylene (PE) and polypropylene (PP) feedstocks will be used to assess the applicability of dehydrogenation and metathesis reactions to these polymers. Light alkane co-reactants used will be n-decane (C₁₀ alkane) and petroleum ether (40 to 60 °C boiling range) to determine the impact of light alkane type on product quality and quantity. Additional parameters to be investigated include reaction time, reaction pressure, light alkane-to-polymer ratio, and catalyst-to-polymer ratio.

The following factors are excluded from the scope of this study:

- Catalyst deactivation rates will not be investigated.
- Catalyst reactivation methods will not be explored.
- No other catalyst types nor combinations other than the Pd/ γ -Al₂O₃ and WO_x/SiO₂ catalyst pairing will be used.
- Catalyst pretreatment methods will also not be varied.

1.5 Outline of dissertation

The structure of this dissertation is illustrated in Figure 1-2.

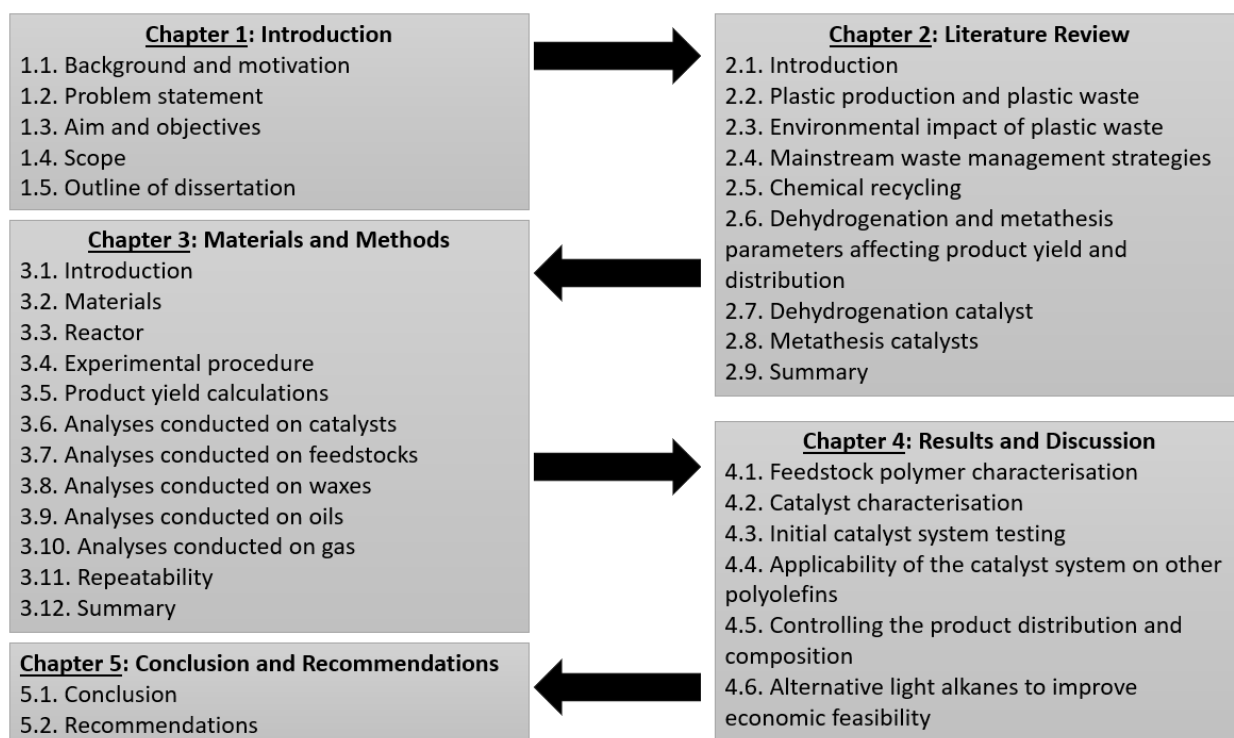


Figure 1-2: Structure of the dissertation

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

Chapter 2 presents a comprehensive review of the literature, beginning with an overview of global plastic production and the consequent generation of plastic waste. Section 2.3 examines the environmental impacts of plastic waste, highlighting the urgency of developing effective waste management strategies. Section 2.4 reviews conventional plastic waste management practices and underscores the need for chemical recycling, particularly for polyethylene (PE) and polypropylene (PP). Section 2.5 summarizes widely studied chemical recycling methods and introduces dehydrogenation and olefin metathesis as emerging alternatives. The remainder of the chapter focuses on prior research concerning the application of dehydrogenation and metathesis to the recycling of PE waste.

2.2 Plastic production and plastic waste

Plastics, also referred to as polymers, were first discovered early in the 20th century and have since surpassed the production rates of most other human-made materials (Wang et al., 2021). Plastic products are relatively inexpensive to manufacture, while being lightweight, durable, flexible, and mouldable (Wang et al., 2021). Due to these traits, plastic products have replaced materials such as glass and metal and are now used in various sectors and industries, including transportation, construction, and healthcare (Gourmelon, 2015).

Since 1950, global plastic production has grown at an annual compound growth rate of 8.4% (Zhang et al., 2021). Furthermore, Zhang et al. (2021) reported that the annual global plastic production in 2018 exceeded 360 million tons and predicted that this could reach 500 million tons by 2025. These global trends are also reflected in the South African plastic market, which experienced an annual compound growth rate of 5% in plastic production. In 2017, South Africa contributed 2.7 million tons to global plastic production.

However, most plastic products are intended for single use, resulting in an annual discard rate of at least 75% (Geyer et al., 2017). Consequently, vast amounts of plastic waste are generated each year, with South Africa producing approximately 2.3 million tons of plastic waste in 2018 (IUCN-EA-QUANTIS, 2020).

2.3 Environmental impact of plastic waste

The durability and non-biodegradable properties of plastics cause them to persist in the environment for hundreds of years, resulting in plastic waste spreading worldwide (Idumah and

Nwuzor, 2019). This persistence is concerning because unmanaged plastic waste contributes to various environmental issues.

The chemical and mechanical weathering of plastic waste leads to the formation of microplastics, which are plastic waste fragments smaller than 5 mm in size. Microplastics are easily ingested by marine organisms; however, this seldom leads to the immediate death of the organism. Rather, these organisms act as vectors for the chemical transfer of pollutants within the food chain (Li et al., 2016).

Adeniran and Shakantu (2020) investigated the impact of unmanaged plastic waste on underdeveloped metropolitan areas in South Africa. They found that the blockage of sewage systems by plastic waste was a common occurrence, which resulted in breeding grounds for mosquitoes and other disease-causing vectors as well as foul odours. Reduced soil aeration and water percolation in surrounding areas were also observed, which caused reduced productivity in agricultural land (Adeniran and Shakantu, 2022). The study also mentioned that these are common occurrences in all developing countries.

Plastics also have numerous toxic constituents such as polyfluorinated chemicals, phthalates, and brominated flame retardants. These compounds leach out, polluting the soil, water, and even air, and have adverse effects on public health (Alabi et al., 2019).

All these environmental concerns can only be addressed through an adequate waste management strategy for plastic waste (Idumah and Nwuzor, 2019).

2.4 Mainstream waste management strategies

Figure 2-1 illustrates the waste management strategies applied in South Africa along with the respective fractions of waste subjected to each method. This will be discussed in the subsequent sections.

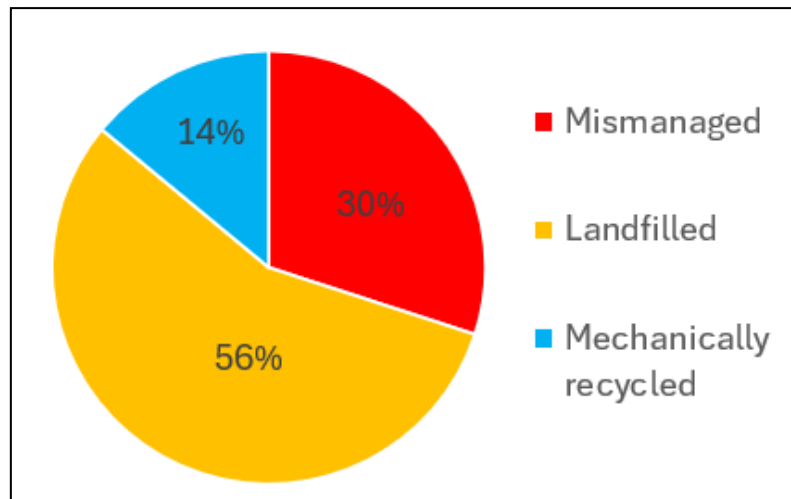


Figure 2-1: Plastic waste management in South Africa (IUCN-EA-QUANTIS, 2020)

2.4.1 Incineration

The open burning of mismanaged plastic waste, conducted solely for waste destruction rather than energy recovery, is a common practice in South Africa. Although specific data is not reported, some estimates suggest that nearly half of the mismanaged plastic waste is eventually incinerated (IUCN-EA-QUANTIS, 2020). Unfortunately, this practice releases numerous hazardous and noxious chemicals such as furans, dioxins, and polychlorinated biphenyls into the atmosphere (Alabi et al., 2019). These chemicals are known to cause damage to the nervous system and organs, as well as irritation to the respiratory tract, eyes, and skin (Alabi et al., 2019). Consequently, more waste is disposed of in landfills than is incinerated.

In developed countries like Sweden, Denmark, and Japan, there are large-scale incinerator facilities that convert solid plastic waste into heat energy for power generation (Ágnes and Rajmund, 2016). However, these facilities also produce harmful pollutants similar to those from open waste burning. Moreover, considering the resources expended in producing polymer products, it is desirable to find more valuable applications for plastic waste (Pan et al., 2020).

2.4.2 Landfilling

Landfilling involves burying waste in layers of earth, and once the designated site reaches capacity, a final cover of soil is applied. Landfilling of plastic waste is still the most common plastic waste management strategy in most countries because it is relatively inexpensive and simple (Huang et al., 2022). In 2018, 80% of plastic waste collected in South Africa, which is approximately 1 million tons, was landfilled (IUCN-EA-QUANTIS, 2020).

However, there are several disadvantages associated with the landfilling of plastic waste. For example, waste is lightweight and therefore easily dispersed from the landfill site to the rest of the environment. Additionally, landfilling uses valuable land for an indefinite period of time (Pan et al., 2020). Landfills have also been identified as sources of microplastics, and it is a common occurrence for toxic additives present in waste to leach into the surrounding groundwater and soil (Siddiqui and Pandey, 2013).

Further contributing to the unsustainable nature of landfilling is the fact that none of the fossil fuel resources used in the production of plastics are recovered (Siddiqui and Pandey, 2013).

2.4.3 Mechanical recycling

In recent years, developed countries have implemented stringent landfill taxes and even bans to mitigate environmental pollution associated with landfills and foster the transition to a more circular plastic economy (Schyns and Shaver, 2021). As a result, the volume of plastic waste undergoing mechanical recycling in Europe doubled from 2006 to 2018, with approximately 10 million tons of plastic waste recycled in 2018 (Schyns and Shaver, 2021).

Generally, mechanical recycling of plastic waste first requires the sorting and separation of the waste according to shape, size, density, and chemical composition. After this, the waste is washed to remove any contaminants before being ground to produce plastic flakes. Finally, new granulates are produced from these flakes by hot melt extrusion (Ragaert et al., 2017). However, the thermal conduction and viscous shearing that the polymers undergo within an extruder result in thermo-oxidative and shear-induced chain scissions, chain branching, and cross-linking of the polymer chains. This chain degradation reduces the polymer's mechanical properties and processability, inevitably making it unusable (Luijsterburg, 2015).

PE and PP are notably prone to various degradation mechanisms. For example, in oxygen-rich environments, thermo-oxidative chain scissions in HDPE lead to an increase in carbonyl concentration, forming stable carbonyl end groups as depicted in Figure 2-2 (Pinheiro et al., 2004).

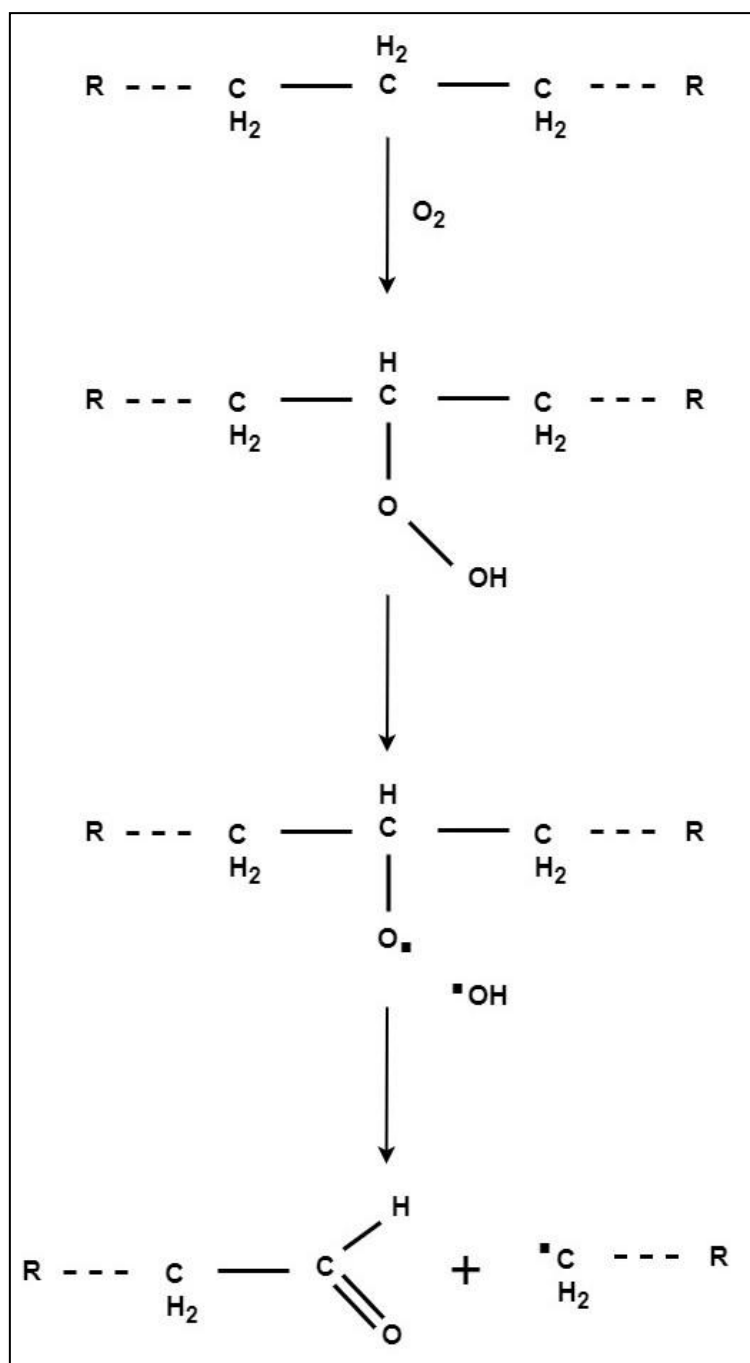


Figure 2-2: Thermo-oxidative degradation pathway of PE

In low-oxygen environments, shear-induced degradation predominates - causing chain scissions and double bond formation (Cuadri and Martín-Alfonso, 2018). LDPE, with its highly branched structure, is particularly susceptible to crosslinking during extrusion, resulting in observed increases in molecular weight (Dordinejad et al., 2018). PP shares a similar radical degradation mechanism with PE; however, thermo-oxidative and thermo-mechanical chain scissions are the primary degradation pathways for PP (Schyns and Shaver, 2021). Consequently, both PE and

PP remain stable for approximately five extrusion cycles before experiencing significant deterioration in polymer performance (da Costa et al., 2005).

Given that the majority of plastic waste comprises of PE and PP, relying solely on mechanical recycling is insufficient to achieve a circular plastic economy (Bodzey and Bánhegyi, 2016).

2.5 Chemical recycling

To address the limitations of mechanical recycling, particularly concerning PE and PP waste, researchers have begun investigating chemical recycling as a viable alternative. Effective chemical recycling could enable the production of valuable feedstocks capable of replacing petrochemicals or even serving as fuels (Thiounn and Smith, 2020).

2.5.1 Pyrolysis

Pyrolysis, sometimes referred to as thermolysis, is defined as the thermal degradation of organic materials in the absence of oxygen (Qureshi et al., 2020). Generally, pyrolysis of plastic waste is performed at 450–600 °C and the products consist of gases, oils, and a solid fraction (Davidson et al., 2021). Furthermore, pyrolysis is a very flexible process and parameters such as reactor type, reaction time, temperature, etc. can all be manipulated to achieve desired product distributions and qualities.

Oil yields range between approximately 50–80 wt.% when pyrolysis is performed on waste PE and PP (Chang, 2023). Researchers also reported that these oils have higher heating values (HHVs) ranging from 35 MJ/kg to as high as 47 MJ/kg, which is comparable to the HHVs of gasoline (43–44 MJ/kg) and diesel (43–46 MJ/kg), suggesting that these pyrolytic-derived oils could be used as an alternative fuel source (Chang, 2023). However, because the PE and PP feedstocks are depolymerised via random bond scissions and chain scrambling, the oils produced contain aromatic compounds as well as alkanes and olefins in the C₆–C₂₀ range (Lee et al., 2021). Consequently, these oils need to be fractionated by distillation if they are to be used as petrochemical feedstocks (Qureshi et al., 2020).

The gases produced through pyrolysis typically consist of mixtures of hydrocarbons C_xH_y (up to C₆) and hydrogen. These gases have reported calorific values ranging between 42–50 MJ/kg, making them suitable as energy sources (Maqsood et al., 2021).

The solid fraction recovered from the pyrolysis of PE and PP waste includes chars and waxes. Char yields increase with higher reaction temperatures, typically comprising 2–4 wt.% of all products, and is predominantly composed of carbon (Maqsood et al., 2021). However, the majority of the solid products are waxes, whose physicochemical properties vary considerably

with the nature of the polymer feedstock. These waxes predominantly consist of saturated and unsaturated hydrocarbons containing approximately 20 to 36 carbon atoms and are commonly subjected to refinery cracking processes for the production of chemicals and fuels (Maqsood et al., 2021).

Currently, industrial-scale application of pyrolysis is still limited with no commercial operating plants noted (Armenise et al., 2021). The main reason is the large amount of energy required for the complete conversion of the polymer feedstock. Efforts have been made to integrate a catalyst into the process to lower the energy requirements; however, these catalysts are expensive and are quickly deactivated (Chang, 2023).

2.5.2 Hydrocracking

Hydrocracking of polymers occurs in the presence of a bifunctional catalyst (acidic support impregnated by a noble or non-noble metal), at 300–450 °C and 2–15 MPa hydrogen pressure. Hydrocracking is sometimes preferred over pyrolysis because it depolymerises the feedstock through carbon-carbon bond cleavage with simultaneous hydrogenation to form mostly saturated liquid products within the fuel range (Munir et al., 2018). Similarly to pyrolysis, a vast number of process conditions and variables can be altered to manipulate the properties of products derived from the hydrocracking of waste polymers.

The oil yields derived from the hydrocracking of PE and PP are normally 80–90 wt.%. At operating conditions of 425 °C, initial hydrogen pressure of 5 MPa, 60-minute reaction time, and utilising the commercial catalyst DHC-8; the oils produced consist mainly of saturated hydrocarbons having boiling points ranging from 60 to 180 °C (Metecan et al., 2005). Due to the desirable composition of these oils, they could potentially be used as feedstock for already existing refinery operations without the need for any preprocessing (Munir et al., 2018).

The gases produced are mixtures of C₁ to C₄ hydrocarbons. However, the process parameters are typically tuned to keep the gas yield below 10 wt.%, as oils are comparatively much more valuable than the derived gaseous products (Liu et al., 2021). Solid yields usually account for less than 3 wt.% of the products produced and consist of partially unreacted polymer fractions along with coke and tar formed on the surface of the catalyst due to additives present in the polymer feedstock (Liu et al., 2021).

Factors currently limiting the practical application of hydrocracking as a plastic waste management strategy are high energy demands, as reaction temperatures are only slightly lower compared to pyrolysis, as well as the high cost of the hydrogen required. Furthermore, process

units must withstand elevated pressure, thereby increasing initial capital costs (Matuszewska et al., 2022).

2.5.3 Solvolysis

Solvolysis entails the thermal depolymerisation of polymers in the presence of suitable solvent molecules. The type of solvolysis is categorised according to the solvent used, where solvolysis using alcohols is termed alcoholysis; likewise, solvolysis where ammonia is used as solvent is called ammonolysis, etc. (Jiang et al., 2022). The presence of a solvent aids in cleaving the polymer feedstock into smaller chains, which in turn lowers the temperature required for complete depolymerisation of the plastic feedstock (Kameel et al., 2022).

Solvolysis reactions are normally carried out at temperatures above 300 °C and as high as 450 °C for approximately 30 to 120 minutes in an inert atmosphere (Kameel et al., 2022). Solvolysis has been shown to be the ideal chemical recycling method to achieve a circular economy for waste polycarbonate (PC) and polyethylene terephthalate (PET), as more than 95 wt.% of these polymer's monomers could be recovered under certain reaction conditions (Jiang et al., 2022).

However, when solvolysis is applied to waste PE and PP, oil yields remain high (above 90 wt.%), but there is no selectivity for a specific component. The oils typically consist of a mixture of saturated and unsaturated aliphatics, cyclics, and aromatics (Kameel et al., 2022). Normally, the oils also have HHVs and H/C ratios in the range of conventional fuels, necessitating the further refinement of the oils (Kameel et al., 2022).

At relatively higher temperatures and longer reaction times, gas yields of about 10 wt.% are reported. It is found that the gas consists of methane, ethene, ethane, propene, propane, butene, and butane. Resultantly, these gases also have commercial value like the oils and can additionally be used as an energy source on-site (Kameel et al., 2022).

When the solvolysis conditions are tuned to maximise oil yields, the solid yield is usually below 5 wt.%. The solids, which are often referred to as chars, consist of unreacted polymer feedstock along with impurities present in the polymers (Kameel et al., 2022).

The lack of selectivity toward a specific product when subjecting waste PE and PP to solvolysis is the main reason for it being an unappealing chemical recycling method for these specific polymers.

2.5.4 Dehydrogenation and metathesis

The need for a chemical recycling method applicable to PE waste that operates at relatively mild reaction conditions while simultaneously delivering a strict product distribution led researchers to investigate tandem dehydrogenation and olefin cross-metathesis (TDOCM) as a possible depolymerisation strategy.

The basic TDOCM process to depolymerise PE using a light alkane is outlined in Figure 2-3. A dehydrogenation catalyst reacts with the polymer and short alkane to introduce an unsaturated bond in both. The metathesis catalyst then facilitates an olefin cross-metathesis reaction around these two unsaturated bonds, resulting in two shorter fragments of the initial polymer chain. These two alkenes then serve as hydrogen acceptors to finally produce two new alkanes (Jia et al., 2016).

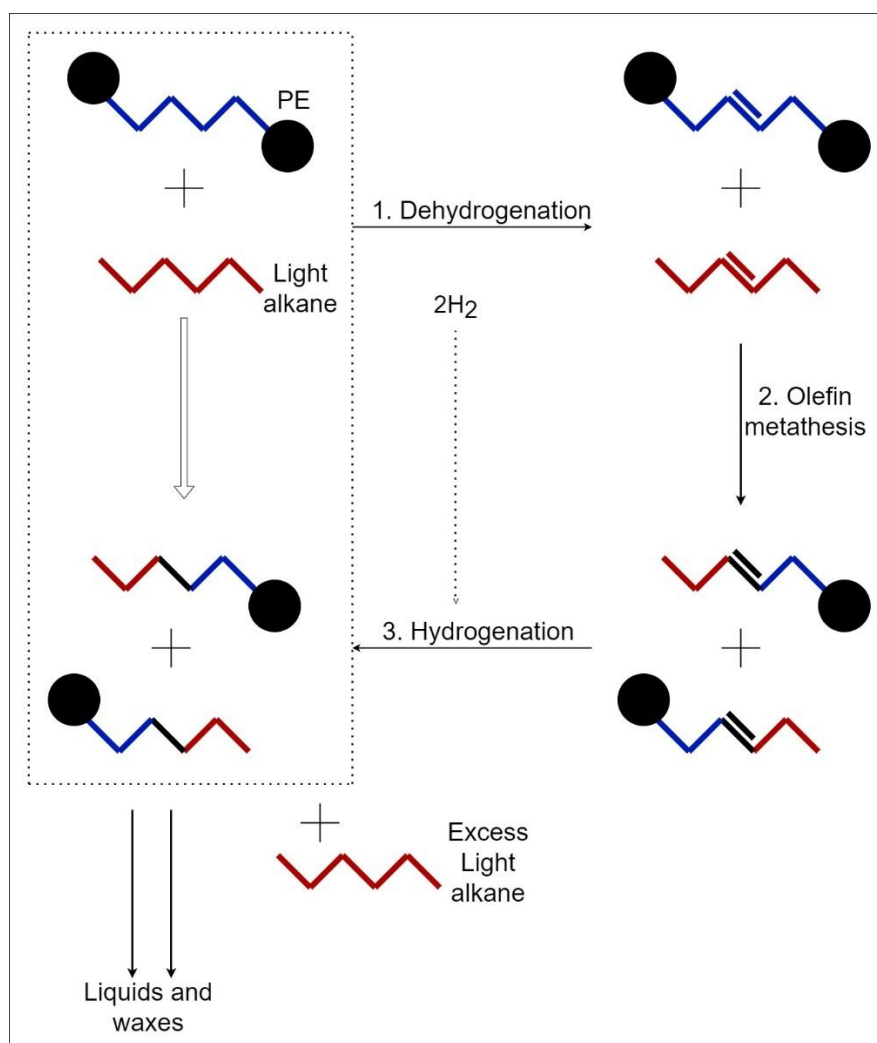


Figure 2-3: Dehydrogenation and metathesis mechanism (Jia et al., 2016)

Goldman et al. (2006) used homogeneous iridium complexes as dehydrogenation catalysts and a Schrock-type metathesis catalyst to convert an n-hexane solution to a mixture of C₂ to C₁₀ alkanes at 125 °C over 24 hours. Although Goldman et al. (2006) wanted to show that TDOCM could be a method for upgrading low-molecular-weight alkanes, they were the first to suggest that TDOCM could also be applied to high-molecular-weight reactants to yield low-molecular-weight products.

More recently, Jia et al. (2016) successfully degraded PE using the same iridium complexes as Goldman et al. (2006) along with Re₂O₇/γ-Al₂O₃ as a heterogeneous metathesis catalyst. Experiments were carried out at 175 °C for 96 hours using n-hexane as co-reactant and produced a distribution of liquid alkane products and waxy solids (Jia et al., 2016).

Continuing the work of Jia et al. (2016), Ellis et al. (2021) developed a fully heterogeneous catalyst system that successfully depolymerised PE to a distribution of liquid and waxy alkanes. SnPt/γ-Al₂O₃ and Re₂O₇/γ-Al₂O₃ were used as the dehydrogenation and metathesis catalysts, respectively, and depolymerisation reactions were performed at 200 °C for 15 hours with n-pentane as co-reactant (Ellis et al., 2021).

Most recently, Kim et al. (2022) showed that WO_x/SiO₂ could be a cheaper and more robust alternative to Re₂O₇/γ-Al₂O₃ as the tungsten oxide-based metathesis catalyst is more stable at higher temperatures. Using a WO_x/SiO₂ and Pt/γ-Al₂O₃ catalyst combination, Kim et al. (2022) successfully depolymerised PE to a distribution of alkane products similar to Jia et al. (2016) and Ellis et al. (2021). However, Kim et al. (2022) achieved these conversions within 3 hours using WO_x/SiO₂ catalysts operating at 300 °C.

Table 2-1 summarises all the existing work conducted on TDOCM of PE.

Table 2-1: Comparison of existing work on the chemical degradation of PE via dehydrogenation and metathesis

Reference	(Kim et al., 2022)	(Ellis et al., 2021)	(Jia et al., 2016)
Olefin metathesis catalyst (metal loading, wt.%), quantity (g)	WO _x /SiO ₂ (2), 0.8	Re ₂ O ₇ /γ-Al ₂ O ₃ (8), 0.5	Re ₂ O ₇ /γ-Al ₂ O ₃ (5), 0.5
(De)hydrogenation catalyst (metal loading, wt.%), quantity (g)	Pt/γ-Al ₂ O ₃ (1.0), 0.5	SnPt/γ-Al ₂ O ₃ (1.7, 0.8), 0.5	Ir complex/γ-Al ₂ O ₃ , 4.2 μmol (Ir basis)
PE, quantity (g)	LDPE, 1.6	HDPE, 0.13	LDPE, 0.12
Short alkane, quantity (g)	n-decane, 9.6	n-pentane, 18.8	n-octane, 2.8
Short alkane/PE ratio (g/g)	6	144.5	23.4
Reaction temperature (°C)	300	200	175
Reaction time (h)	3	15	96
Molecular weight of virgin PE (kDa)	M_n	9.1	17.9
	M_w	75.2	52.8
	D	8.3	2.9
Molecular weight of wax (kDa)	M_n	0.68	2.6
	M_w	0.84	14.2
	D	1.2	5.5

2.6 Dehydrogenation and metathesis parameters affecting product yield and distribution

Although the type and amount of catalyst used are the predominant factors affecting the yield and distribution of products produced from the TDOCM of PE waste, several other process parameters also notably influence the characteristics of the derived products, such as PE type, the light alkane used and reaction time.

2.6.1 Polymer type

PE can be subdivided into three groups, namely, high-density polyethylene (HDPE), low-density polyethylene (LDPE), and linear low-density polyethylene (LLDPE). In their study, Jia et al. (2016) individually subjected all three polymers to TDOCM using Re₂O₇/γ-Al₂O₃ and iridium complexes as catalysts at 175 °C for 96 hours. The oil yield was observed to increase with a decrease in the molecular weight (MW) of the polymer, as HDPE (MW = 365 000 g/mol) yielded an oil fraction of 62%, but LDPE (MW = 97 700 g/mol), and LLDPE (MW = 74 000 g/mol) yielded oil fractions of 86% and 77% respectively. Although higher MW polymers produce lower oil fractions, the composition of the oils seems to be mostly unaffected by the PE type (Jia et al., 2016).

Commercial PE frequently contains various additives such as zinc stearate, as well as polyphenol- and phosphite-based stabilisers that modify the properties of PE (Jia et al., 2016). To study the effect of these additives, Jia et al. (2016) subjected an HDPE (MW = 124 000 g/mol) sample, containing the aforementioned additives, to TDOCM. No notable impact on the quantity and composition of the oil produced could be detected compared to a control experiment (Jia et al., 2016).

2.6.2 Light alkane used as solvent

TDOCM is performed in the presence of a large excess of a light alkane relative to the PE. This minimises the possibility of redundant metathesis between two PE chains, which would not result in the effective breakdown of the polymer (Jia et al., 2016). To date, n-pentane, n-hexane, n-heptane, n-octane, and n-decane have been used as solvents for PE TDOCM (Kim et al., 2022).

Kim et al. (2022) investigated how product yield and composition are affected when the solvent is switched from n-heptane to n-decane. Experiments with n-decane showed higher reaction rates compared to those with n-heptane. This difference was attributed to the phase difference of the two solvents at the reaction temperature of 300 °C: n-heptane is a supercritical fluid, whereas n-decane remains a liquid (Kim et al., 2022). Similarly, Jia et al. (2016) observed the same phenomenon when switching from n-pentane to n-hexane and postulated that the increased reactivity could be due to PE having higher solubility in liquids than in supercritical fluids. Furthermore, Kim et al. (2022) also noted that using n-decane shifts product selectivity towards higher-molecular-weight alkanes.

2.6.3 Reaction time

Longer reaction times lead to a more complete breakdown of the PE feedstock and a narrower MW distribution in the products, as more scission and fragmentation reactions occur at extended periods of time (Jia et al., 2016). Furthermore, Jia et al. (2016) also observed that the initial breakdown is rather rapid, with no parent PE material remaining after just 2 hours. However, after these 2 hours, 81% of the products are still waxes, and it was only after an additional 22 hours of reaction time that the oil yield overtook the wax yield (Jia et al., 2016). Kim et al. (2022) report the same trend: oil yields increase over time, whilst wax yields decrease. Interestingly, however, for the longer reaction times studied, the formation of higher MW compounds ($>C_{16}$) in the oils was favoured.

2.6.4 Catalyst pretreatment

Generally, catalyst pretreatment involves dehydrating both the metathesis and the dehydrogenation catalysts under a flow of an inert gas, such as helium, at 450 to 500 °C for 1 to 2 hours.

Ellis et al. (2021) noticed that when SnPt/ γ -Al₂O₃ and Re₂O₇/ γ -Al₂O₃ were physically mixed before pretreatment, these catalysts would demonstrate more than double the reactivity of the same catalysts that were pretreated separately. Apart from this observation, no further investigations on the effect of catalyst pretreatment conditions on product yield and quality were reported.

2.7 Dehydrogenation catalysts

The dehydrogenation catalyst removes hydrogen from both the PE chain and the light alkane. Following metathesis, hydrogenation of the newly formed alkene produces saturated alkanes. The first dehydrogenation catalysts shown to successfully depolymerise PE via TDOCM were supported “pincer”-ligated iridium complexes reported by Jia et al. (2016). More specifically, Brookhart's bis(phosphinite) ligated (^t-BuPOCOP)Ir complex was reported to deliver the highest oil yields, as this catalyst favours the production of internal alkenes, which degrades PE chains more effectively (Jia et al., 2016). These Ir-based catalysts, however, are homogeneous, which will complicate catalyst recovery, compared to heterogeneous catalysts, if TDOCM were ever to be applied on an industrial scale.

The alternative heterogeneous dehydrogenation catalysts Pt/ γ -Al₂O₃, SnPt/ γ -Al₂O₃ and Pd/ γ -Al₂O₃ used by Ellis et al. (2021) proved to be just as effective in TDOCM reactions as the Ir-based catalyst. Most notably, Pd/ γ -Al₂O₃ exhibited the highest surface area activity, with an activity 4 times that of Pt/ γ -Al₂O₃ and SnPt/ γ -Al₂O₃, with all three catalysts producing oils of nearly identical compositions (Moore, 2024).

2.8 Metathesis catalysts

Currently, two metathesis catalysts have been shown to successfully depolymerise PE by TDOCM. The first study using Re₂O₇/ γ -Al₂O₃ was reported by Jia et al. (2016) and later by Ellis et al. (2021). However, both of these research groups indicated that there is a challenge in kinetically coupling the dehydrogenation and metathesis reactions such that the system features high activity and stability. This is because non-oxidative alkane dehydrogenation requires temperatures in excess of 400 °C, however, the active sites on the Re-based metathesis catalyst become unstable once temperatures start to exceed 100 °C (Jia et al., 2016). Consequently, Jia

et al. (2016) and Ellis et al. (2021) settled on reaction temperatures of 175 °C and 200 °C, respectively, resulting in reaction times of 15 to 96 hours.

Kim et al. (2022) expressed the same issue with $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$ and also noted that this catalyst is difficult to regenerate. Alternatively, they suggested using silica-supported tungsten oxide (WO_x/SiO_2) as the metathesis catalyst. The increased thermal stability of WO_x/SiO_2 allowed the researchers to operate at temperatures of 300°C, thus only requiring reaction times of 2 to 3 hours as the kinetics are more favourable at these higher temperatures. Additionally, rhenium is 100 times more expensive than tungsten, thus WO_x/SiO_2 would also improve process economics. However, WO_x/SiO_2 is easily deactivated by oxygenates, but Kim et al. (2022) managed to prevent substantial catalyst deactivation by adding 4 Å zeolite to the reactor contents.

2.9 Summary

After considering the existing work, $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ and WO_x/SiO_2 have been chosen as the dehydrogenation and metathesis catalysts, respectively, in this study, with zeolite (4 Å) also present to protect the WO_x/SiO_2 from any oxygenates. This catalyst combination is fully heterogeneous and can operate in conditions where process kinetics are more favourable, potentially improving process economics. Given this choice of catalyst, reaction times of 3 hours and reaction temperatures of 300 °C will be the starting point of this study. Solvents that will be investigated in this study include n-decane and petroleum ether, which is a petroleum fraction that boils in the 40 to 60°C range; they consist mostly of aliphatic hydrocarbons (pentanes and hexanes) and are more widely available and significantly less expensive than n-decane.

Currently, there are large gaps in the literature regarding the effect of temperature, catalyst loading ratios, polymer-to light-alkane ratios, and reaction pressure on the quantity and quality of products obtained. This study aims to address these shortcomings and to determine whether the degradation scheme could be applied to PP as well.

CHAPTER 3 MATERIALS AND METHODS

3.1 Introduction

Chapter 3 starts by detailing the materials used in this study. This is followed by a description of the experimental setup and procedure, which also elaborates on the catalyst synthesis, product recovery, and the analyses conducted on the products. The chapter concludes by discussing the repeatability of the experimental procedure.

3.2 Materials

Table 3-1 summarises the materials and reactants utilised in this study, along with their respective supplier and purities.

Table 3-1: Materials and reactants utilised in this study

Material	Use	Supplier	Purity
n-Decane	Light alkane feedstock	Merck	≥95%
Petroleum ether (40 to 60 °C boiling range)	Light alkane feedstock	Minema	≥99.0%
p-Xylene	Solvent	Minema	≥98.5%
Dichloromethane	Solvent	Minema	≥99.0%
Virgin HDPE	Polymer feedstock	Merck	-
Virgin LDPE	Polymer feedstock	Merck	-
Virgin PP	Polymer feedstock	Merck	-
Recycled PP	Polymer feedstock	Potchefstroom Plastic	-
Recycled PE	Polymer feedstock	Potchefstroom Plastic	-
SiO ₂ ; average pore size 60 Å (52-73 Å), 70-230 mesh	Catalyst synthesis	Sigma-Aldrich	-
(NH ₄) ₆ H ₂ W ₁₂ O ₄₀ ·xH ₂ O	Catalyst synthesis	Merck	≥99.99%
Pd/γ-Al ₂ O ₃	Catalyst	Merck	-
Molecular sieves, 4 Å	Adsorbent	Sigma-Aldrich	-

3.3 Reactor

The tandem dehydrogenation and olefin cross metathesis (TDOCM) reactions were performed in a 600 mL batch autoclave reactor obtained from the Parr Instrument Company. A schematic depicting the reactor can be seen in Figure 3-1.

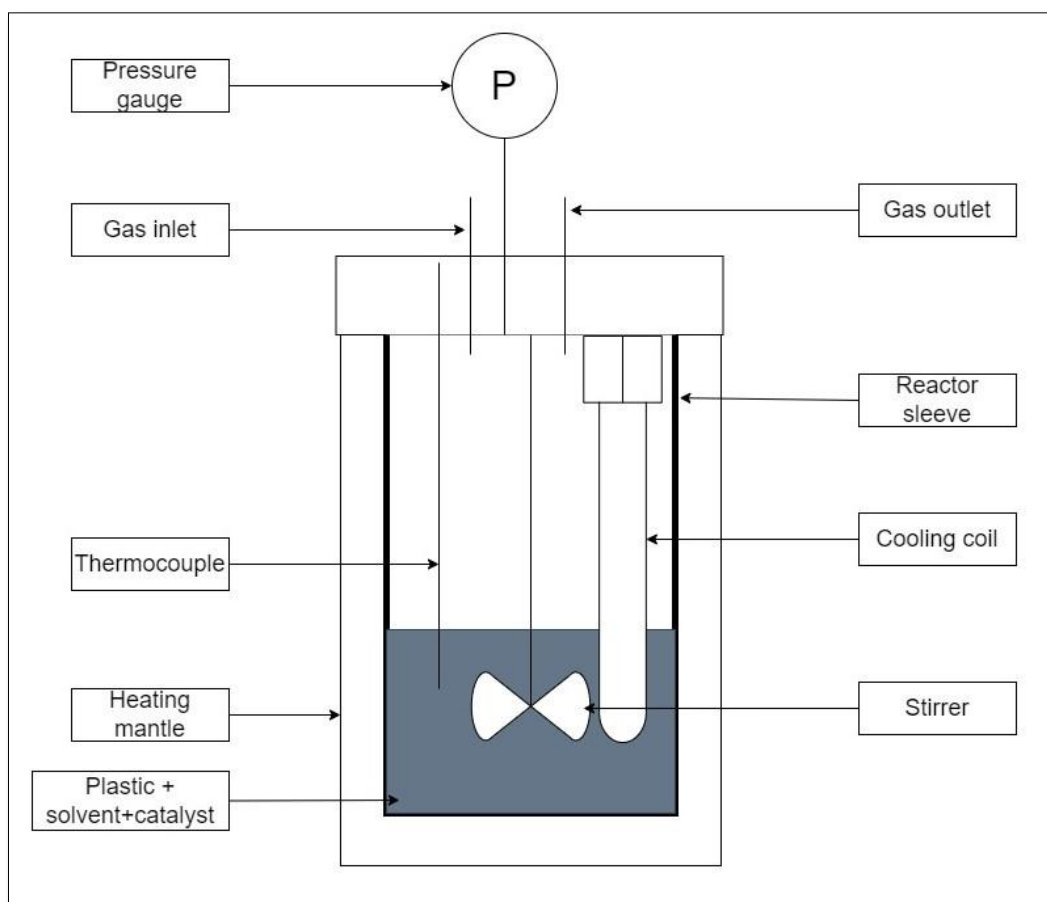


Figure 3-1: 600 mL batch autoclave reactor from Parr Instrument Company

3.4 Experimental procedure

A block diagram summarising the general experimental procedure can be seen in Figure 3-2.

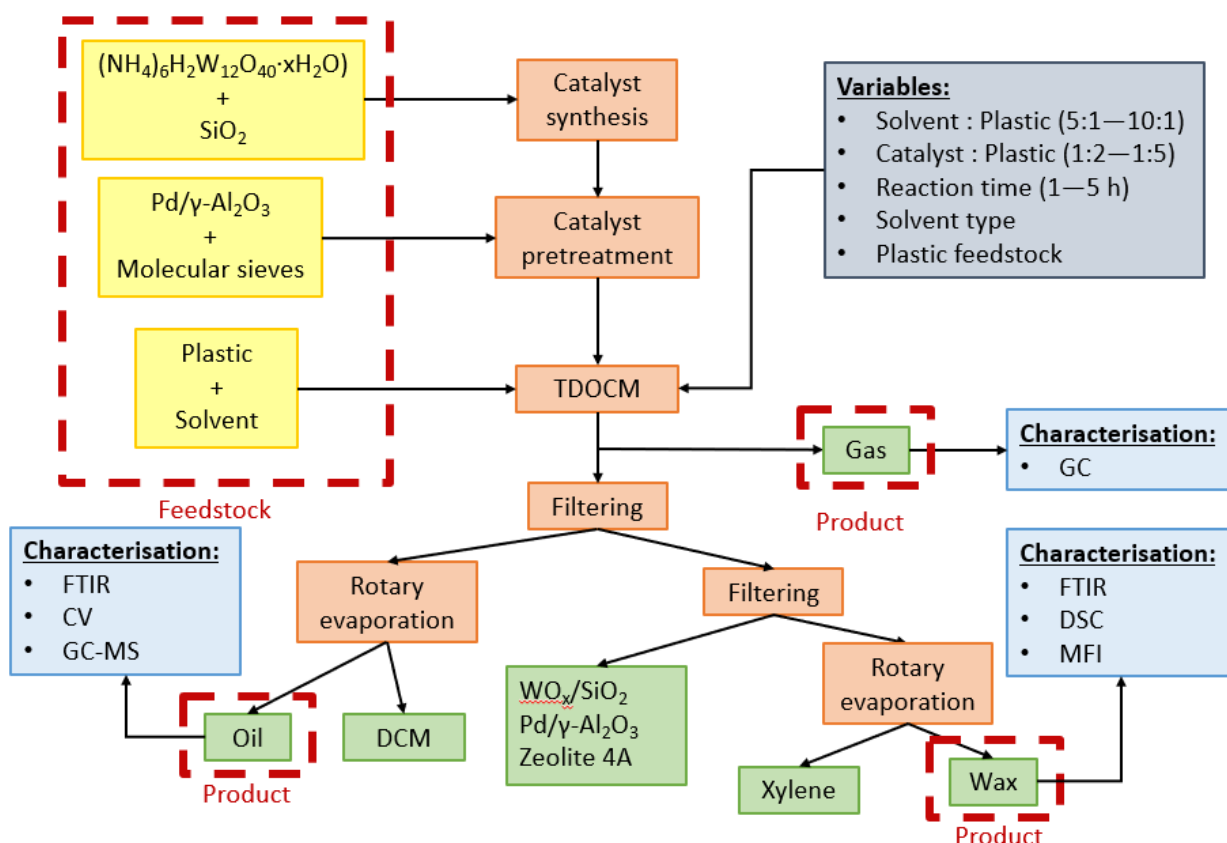


Figure 3-2: Block diagram of the general experimental procedure

3.4.1 Catalyst synthesis

The WO_x/SiO_2 (2 wt.%) olefin metathesis catalyst was prepared by a wet impregnation technique detailed by Kim et al. (2022). First, 6.4 g of 4.7 mM ammonium meta-tungsten hydrate $((\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O})$ solution was added dropwise to 4.0 g of silica support (SiO_2) and mixed for 10 minutes. This mixture was then dried at 120 °C for 24 hours in an oven. Finally, the dried ammonium meta-tungsten hydrate and silica support mixture was removed from the oven and placed in a muffle furnace at 120 °C for 2 hours and then calcined at 500 °C for 12 hours using a ramp rate of 3 °C/min in static air.

Molecular sieves (4 Å) were activated by heating from ambient temperature to 310 °C at a ramp rate of 1 °C/min and then holding at 310 °C for 15 hours under static air. The activated molecular sieves were then stored in an airtight container before use. $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ (0.5 wt.%) was purchased from Merck and used as received.

3.4.2 Catalyst pretreatment

The WO_x/SiO_2 , $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$, and the molecular sieves were mixed prior to being placed in the Parr reactor. This mixture was then dehydrated at 450 °C for 2 hours, including a ramping period

(10°C/min), under a 300 ml/min flow of nitrogen. After this period the reactor was left to cool to room temperature before polymers and decane were added.

3.4.3 General procedure for TDOCM reactions

Following the catalyst pretreatment step, approximately 5 g of plastic was accurately weighed off and placed into the reactor sleeve along with the corresponding amount of decane to achieve the desired plastic-to-decane weight ratio.

The reactor was then purged and pressurised to 5 bar using nitrogen gas. After this, the reactor was heated to the desired temperature at a heating rate of 10 °C/min using a heating mantle controlled by a controller supplied by the Parr Instrument Company. Once the reactor reached the set temperature, that temperature was maintained for the desired reaction time. After the TDOCM experiment was conducted for the desired reaction time, the reactor was cooled to 25 °C using the cooling coil fitted to the reactor. Once the reactor cooled, the final pressure within the reactor was noted.

3.4.4 Product recovery

After completion of the TDOCM reaction, gas products in the reactor headspace were transferred to a gas sampling bag via the gas outlet valve fitted to the reactor. Excess pressure was then vented and the reactor sleeve containing catalysts, waxes, and liquid products was removed.

The reactor sleeve was thoroughly rinsed with dichloromethane (DCM) to remove all waxes, catalysts, and liquid products. The DCM and the product mixture were then subjected to vacuum filtration to separate the solids and liquids. The oil product and the DCM mixture were then placed in a rotary evaporator and heated to 60 °C under atmospheric pressure, allowing the DCM to evaporate from the oil product, after which it was weighed.

p-Xylene was added to the wax and catalyst fraction, and the mixture was heated to 90 °C to allow the waxes to dissolve. It was then filtered to separate the catalyst from the wax products. The xylene and wax mixture were then placed in a rotary evaporator and heated to 60 °C at 25 mbar pressure, allowing the xylene to evaporate from the wax products, which could then be weighed.

3.5 Product yield calculations

3.5.1 Gas yields

The mol amount of nitrogen present in the reactor at the start of the run, after the reactor was purged and pressurised with nitrogen, was calculated as follows:

$$n_N = \frac{P_{initial} \times V}{R \times T} \quad \text{Eq. 1}$$

Where:

$P_{initial}$ is the absolute pressure inside the reactor at the start of the run and V refers to the volume of the reactor in dm^3 . T is the temperature in Kelvin and R the universal gas constant in $\text{L}\cdot\text{atm}/\text{mol}\cdot\text{K}$.

The total mole amount of gas produced at the end of the TDOCM experiments were calculated as follows:

$$n_T = \frac{P_{end} \times V}{R \times T} - n_N \quad \text{Eq. 2}$$

The mole fraction of each component present in the produced gas can be obtained from GC TCD/FID analysis. Utilising this, the mass of each compound present in the gas was calculated as follows:

$$m_i = x_i \times n_T \times MW_i \quad \text{Eq. 3}$$

Where:

The subscript i refers to either methane, ethane, propane, or butane. x_i is the mol fraction obtained from GC analysis and MW_i is the molecular weight of each respective compound. Thus, the total mass of gas produced is the sum of the mass of each individual component as follows:

$$m_{gas} = m_{CH_4} + m_{C_2H_6} + m_{C_3H_8} + m_{C_4H_{10}} \quad \text{Eq. 4}$$

Finally, the gas yield was calculated as follows:

$$gas\% = \frac{m_{gas}}{m_{solvent(cons.)} + m_{plastic}} \times 100 \quad \text{Eq. 5}$$

Where:

$m_{plastic}$ refers to the mass of plastic inserted into the sleeve of the reactor at the start of the DCAM reaction and $m_{solvent(cons.)}$ was calculated according to Equation 6.

$$m_{solvent(cons.)} = m_{solvent(init.)} - m_{solvent(final)} \quad \text{Eq. 6}$$

Where:

$m_{solvent(init.)}$ refers to the mass of decane initially inserted into the reactor and $m_{solvent(final)}$ refers to the mass of unreacted decane remaining in the reactor after the DCAM reaction was completed. $m_{solvent(final)}$ was calculated using the GC-FID method described in Section 3.8.3.

3.5.2 Liquid yields

The oil yield was calculated as follows:

$$oil\% = \frac{m_{liquid} - m_{decane(final)}}{m_{decane(consumed)} + m_{plastic}} \times 100 \quad \text{Eq. 7}$$

Where:

m_{liquid} refers to the weight of the liquid product recovered from the reactor after the TDOCM reaction and after rotary evaporation to remove the DCM.

3.5.3 Wax yields

The wax yield was determined as follows:

$$wax\% = \frac{m_{wax}}{m_{decane(consumed)} + m_{plastic}} \times 100 \quad \text{Eq. 8}$$

Where:

m_{wax} refers to the weight of the wax products after filtering and rotary evaporation to remove the xylene. Thus, all yields are calculated from the amount of decane consumed and do not include unreacted decane as part of the oil yield.

3.6 Analysis of dehydrogenation and olefin metathesis catalysts

3.6.1 X-ray fluorescence (XRF)

The chemical composition of the dehydrogenation and metathesis catalysts, before and after pretreatment, was determined through X-ray fluorescence analyses (XRF). XRF was performed

by Bureau Veritas Testing and Inspections South Africa according to standard D4326 defined by the American Society for Testing and Materials (ASTM). This analysis was performed merely to assess whether the catalyst pretreatment step affected the chemical composition of the catalysts in any way.

3.6.2 N₂ low-pressure adsorption analysis

Nitrogen adsorption measurements were performed in-house to determine the surface area, pore size distribution, and porosity of the catalyst samples, using a Micrometrics ASAP 2010 instrument. Prior to analysis, the samples were degassed under vacuum at 90 °C for 1 hour, followed by 300 °C for 6 hours, to remove any adsorbed moisture or contaminants, ensuring clean surface conditions for accurate measurements. The degassed samples were then cooled to 77 K using liquid nitrogen. Nitrogen gas was introduced incrementally, and the amount adsorbed by the sample was recorded across a range of relative pressures (P/P_0 from approximately 0.05 to 1.0) to generate an adsorption isotherm, and the data were acquired using ASAP 2020 v4.0 software. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method, which analysed the linear portion of the adsorption isotherm. The slope and intercept of the BET plot were used to determine the monolayer adsorption capacity, which was then converted to surface area. The pore size distribution and pore volume were determined by analysing both adsorption and desorption branches of the isotherm using the Barrett-Joyner-Halenda (BJH) model. This method provided information on mesopore size distribution (2–50 nm) and cumulative pore volume.

3.6.3 X-ray Diffraction (XRD)

Qualitative XRD analysis was conducted on the dehydrogenation and metathesis catalysts, both before and after pretreatment, to evaluate if the catalyst pretreatment step affected the catalysts' crystalline structure or phase compositions. The catalysts were prepared for XRD analysis using a back-loading preparation method. Diffractograms were obtained using a Malvern Panalytical Aeris diffractometer with a PIXcel detector and fixed slits with Fe-filtered Co-K α radiation. The phases were identified using X'Pert Highscore Plus software. The relative phase amounts (wt.%) were estimated using the Rietveld method. XRD analysis was performed by XRD Analytical and Consulting.

3.6.4 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS)

The surface morphology of the catalyst samples, both before and after pretreatment, was analysed using SEM to observe structural features and particle sizes. Catalyst samples were

carefully prepared by mounting them onto aluminium stubs using double-sided carbon tape to prevent movement during imaging. SEM imaging was conducted with a FEI QUANTA 250 FEG using a backscattered electron compositional signal under high-vacuum conditions. The accelerating voltage was set to 15 kV, at a working distance of approximately 10 mm, and a 300 ns scan speed to achieve optimal resolution for surface characterisation. Multiple images were taken at various magnifications to capture both the general morphology and finer surface details of the catalyst particles. Images were saved for subsequent analysis and comparison.

Elemental analysis of the catalyst samples was performed using EDS in conjunction with SEM. The OXFORD X-max EDS detector, integrated with the SEM system, was used for elemental analysis. The same operating conditions as the SEM imaging were applied to ensure consistency. Point, line, and area scans were conducted on selected regions of the catalyst samples to identify elemental composition. An accelerating voltage of 15 kV was used to optimize the detection of elements in the sample. The acquired EDS spectra were analysed to determine the elemental composition of the catalyst surface. The system used a semi-quantitative approach, as it relied on a spectral library pre-programmed by the manufacturer that provided approximate elemental quantification based on characteristic X-ray peaks. Both SEM and EDS were performed in-house.

3.7 Analysis of polymer feedstocks

3.7.1 Melt Flow Index (MFI)

MFI experiments were conducted at Potch Plastics on all polymer feedstocks. Approximately 20 g of the polymer sample was dried at 80 °C for 24 hours to remove moisture. The MFI measurements were conducted using a melt flow indexer preheated to 190 °C. The polymer sample was loaded into the barrel of the melt flow indexer, where it was allowed to equilibrate at the set temperature for 5 minutes to ensure uniform melting. A standard weight of 2.16 kg was applied to the piston. Under the applied load, the molten polymer was extruded through a capillary die. The extrudate was collected over a period of 10 minutes, and the mass of the material collected was recorded. Finally, the MFI, expressed in grams per 10 minutes (g/10 min), was calculated by dividing the mass of the extrudate by the duration of the test.

3.7.2 Gel Permeation Chromatography (GPC)

GPC was used to determine the number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI) of the polymer feedstocks using a PerkinElmer Flexar FX-20. The samples were dissolved in 1,2,4-trichlorobenzene (TCB) at room temperature to prepare a solution with a concentration of 1 mg/mL. The solution was filtered through a 0.45 µm syringe filter to remove any particulates that could interfere with the analysis.

GPC analysis was conducted using a system equipped with a refractive index (RI) detector. The two MIXEDB GPC columns, connected in series, were calibrated with polystyrene standards of known molecular weights (1050–1 150 000 g/mol) to create a calibration curve for accurate molecular weight determination, which can be seen in Appendix B. The mobile phase was 1,2,4-trichlorobenzene at a flow rate of 1.0 mL/min, and the column temperature was maintained at 90°C to ensure optimal separation and resolution. The elution times of the sample were recorded, and the molecular weight distribution was calculated by comparing retention times with the polystyrene calibration curve. GPC software was used to calculate number average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI) from the chromatographic data, based on the relative sizes of the polymer molecules.

3.7.3 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was performed in-house to provide insight into the thermal transitions and crystallinity of the samples.

Thermal analysis was conducted using an SDT Q600 TGA instrument. Approximately 15 mg of the sample was weighed off and placed in the TGA furnace. Initial equilibrium was set at 25 °C, after which the sample was heated to 300 °C at a rate of 10 °C/min under continuous nitrogen (99.999% purity) flow of 100 mL/min. Additionally, the Flory equation, as seen in Equation 9, was used to estimate the number average molecular weights (M_n) of the samples in g/mol (Blaine and Waguespack, 2001).

$$M_n = \frac{K}{1 - \left(\frac{T_m}{T_{m_0}}\right)} \quad (9)$$

Where K is a polymer-specific constant 1,000–3,000 g/mol for HDPE and 1,000 to 1,500 g/mol for LDPE. T_{m_0} is the equilibrium melting temperature of the polymer (414 K and 408 K for HDPE and LDPE, respectively) and T_m is the observed melting temperature of the sample observed as the peak of the endothermic transition.

3.8 Analysis of wax products derived from TDOCM experiments

3.8.1 Fourier-transform infrared (FTIR) spectroscopy

In-house FTIR spectroscopy was employed for the characterisation of waxes. A BRUKER ALPHA-P attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectrometer was utilized for solid-state analyses. OPUS version 6.0 (BRUKER software) was used for spectrum

acquisition and processing. The FTIR spectra were captured with a wavelength range of 4000–400 cm^{-1} .

3.8.2 Gel Permeation Chromatography (GPC)

GPC was also performed on the wax products according to the same procedure described in Section 3.7.2.

3.8.3 Differential Scanning Calorimetry (DSC)

DSC was also performed on the wax products according to the same procedure described in Section 3.7.3.

3.9 Analysis of liquid products from TDOCM experiments

3.9.1 Fourier-transform infrared (FTIR) spectroscopy

FTIR spectroscopy was also used to characterise the oil products, and the same procedure as previously outlined for the wax products in Section 3.7.1 was followed for the oil products.

3.9.2 Gas Chromatography-Mass Spectrometry (GC-MS) and Gas Chromatography-Flame Ionisation Detector (GC-FID)

Two distinct in-house gas chromatography (GC) methods were employed to thoroughly characterise the components and composition of the oil product. The first method utilised an MS detector, allowing for the qualitative identification of all components within the oils. The second method incorporated an FID, enabling precise quantification of the amount of decane present in the oils.

GC-MS

Firstly, a 0.01 g sample was dissolved in 1 ml of hexane, in triplicate, after the samples were inserted into GC vials with a surgical injector fitted with a 0.22 μm pore size syringe filter.

To identify the components present within the oil product, an Agilent 7890 gas chromatograph equipped with an Agilent 5975 triple-axis mass-selective detector was used. The GC was fitted with a 30 m x 0.25 mm x 0.1 μm J&W HP-5ms column. The injection volume of the sample was 1 μL with a split ratio of 5:1, using Helium as carrier gas at a column flow of 1 mL/min. The initial oven temperature was set at 45 °C and held for 5 min, after which the temperature was ramped at 8°C/min to 325 °C and held for 20 min. The inlet and transfer line temperatures were set at 250

°C and 280 °C, respectively. The MS source and quad temperatures were 230 °C and 150 °C, respectively. Peaks were identified using the NIST 11 mass spectra library.

GC-FID

Firstly, a 0.01 g sample was dissolved in 1 ml hexane, in triplicate, after which 100 µl internal standard (Methyl laurate) was added. Finally, the samples were inserted into GC vials using a surgical injector fitted with a 0.22 µm pore size syringe filter.

Samples were then analysed using an Agilent 7820A GC with an FID detector. The GC was fitted with a 5 m x 0.535 mm x 0.15 µm DB-HT-SimDis column. 1 µL of sample was injected with a split ratio of 40:1 at 250 °C at the inlet. The initial oven temperature was 40 °C for 0.5 min, after which the temperature was increased at 10°C/min to 200 °C, held for 10 min, and then at 35 °C/min to 400 °C.

The percentage decane in each sample was determined by external calibration of the GC-FID. Decane standards of different concentrations were prepared with a constant concentration of internal standard (Methyl laurate). A linear calibration curve was obtained, which was used to calculate the concentration of decane in the subsequent samples. The calibration curve is shown in Appendix B.

3.9.3 Calorific Value (CV)

The calorific value (CV) of the oil product (expressed in MJ/kg) was determined to evaluate its energy content. The analysis was performed using a CV IKA C5003 calorimeter. Samples were prepared by filling the sampling cup with 1.5 g of oil, after which they were loaded into the combustion chamber of the calorimeter, ensuring proper sealing. The calorimeter was then charged with oxygen to support complete combustion. The sample was ignited electrically, and the heat released during combustion was absorbed by the surrounding water jacket. The rise in temperature of the water jacket was recorded over time using a high-precision thermocouple integrated into the calorimeter. The system's heat capacity was calibrated using benzoic acid to relate the temperature change to the energy released by the sample.

3.10 Analysis of gaseous products derived from DCAM experiments

3.10.1 Gas Chromatography (GC)

The composition of the gas products was determined by GC using a PerkinElmer Clarus 500 GC apparatus. The GC was fitted with two columns, a J&W HP-PLOT/Q (30 m x 0.535 mm) from Agilent and an Elite GC GS MSIEVE (30 m x 0.53 mm) from PerkinElmer. These two columns

were then interconnected to the sample loop, thermal conductivity detector (TCD), and flame ionization detector (FID) via a VICI 10-port gas sampling valve from Valco Instruments. Argon (purity > 99.999 %, Afrox) was used as carrier gas with an initial flow rate of 4 mL/min, ramped to 12 mL/min after 25 minutes. The thermal conductivity detector (TCD) was set to 200 °C. The oven temperature was set at 60 °C and the system was calibrated for CO₂, CO, H₂, CH₄, C₂H₄, C₂H₆, C₃H₈, C₄H₁₀, O₂, and N₂ analysis. CO₂ was separated out in the J&W HP-PLOT/Q column, and a valve switch prevented it from entering the Elite GC GS MSIEVE column. Data processing was then conducted using TotalChrom Navigator software, and the concentration of each component was determined using their individual peak areas on the chromatogram.

3.11 Repeatability

In Appendix A, Tables A-1 and A-2, the yields of each product fraction from repeat experiments are summarised. A confidence interval for each product fraction was calculated using Equation 10.

$$CI = \bar{x} \pm (t_{score} \times \frac{\sigma}{\sqrt{n}}) \quad \text{Eq. 10}$$

Where:

$\bar{x}$ refers to the sample mean, σ is the standard deviation and n is the sample size (in this case, 3). $t_{score} = 4.303$ for 2 degrees of freedom and a 95% confidence level.

Similarly, a confidence interval for quantifying the amount of decane present in the oil fraction was also calculated using Equation 10. This is summarised in Table A-3 of Appendix A.

Finally, an overall uncertainty, based on a confidence level of 95%, could be calculated using Equation 11. Thus, the confidence interval reported for the product yields reflects the uncertainty associated with the TDOCM experimental method as well as the decane quantification method.

$$Total\ uncertainty = \sqrt{(Uncertainty_1)^2 + (Uncertainty_2)^2} \quad \text{Eq. 11}$$

Where:

Uncertainty₁ and Uncertainty₂ refer to the uncertainties associated with the experimental method and the decane quantification step, respectively.

3.12 Summary

A batch autoclave reactor was used for the TDOCM of various PE and PP feedstocks along with decane acting as a light alkane in the reaction. The reaction parameters that were investigated include the catalyst-to-polymer loading ratio, light alkane-to-polymer ratio, reaction time, and the composition of the polymer feedstock.

A summary of the overall experimental method is depicted in Figure 3-2. Firstly, a metathesis catalyst was prepared following similar methods as detailed in the related literature. Then, the catalyst system underwent a pretreatment step before commencement of the TDOCM reactions. After the reactions, the oil and wax products were separated by a series of filtration and rotary evaporation steps using the appropriate solvents.

The gas produced underwent GC analysis whilst the oil product was subjected to FTIR, GC-MS, GC-FID, and CV analysis. The wax products were characterised using GPC, DSC, and FTIR spectroscopy.

The gas yield was calculated from the ideal gas law and data from GC analysis. The oil and wax yield were calculated directly by weighing each of these product fractions. The product yields reported were calculated from the amount of decane consumed and do not include unreacted decane as part of the oil product.

Finally, the repeatability of the experimental method was investigated, and an error based on a confidence interval of 95% was calculated.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Feedstock polymer characterisation

Table 4-1 summarises the polymer type, grade, number average molecular weight (M_n), and melt flow index (MFI) of the various polymer samples utilised in this study

Table 4-1: Characteristics of polymers subjected to TDOCM experiments

Sample ID	Polymer type	Grade	M_n (g/mol)	MFI (g/10min)
HDPE_V	PE	Virgin	165 000	14
LDPE_V	PE	Virgin	30 000	32
PP_V	PP	Virgin	67 000	9
PE_C	PE	Consumer	276 000	15
PP_C	PP	Consumer	n.d.	10
PE_R	PE	Recycled	87 000	0.5
PP_R	PP	Recycled	n.d.	8

The majority of TDOCM experiments were conducted using HDPE_V, LDPE_V, and PP_V, as these three samples were virgin grade and thus would not contain any fillers, pigments, or thermal stabilisers, thereby reducing the number of variables when investigating how other reaction parameters influence product distribution and quality. These virgin polymers were also specifically chosen because their molecular weights are in line with common consumer-grade examples, meaning they will more accurately simulate how TDOCM will perform as a potential recycling scheme. Additionally, the virgin polymer samples used in this study have considerably higher molecular weights (3 to 10 times greater) than polymers investigated in other studies (Kim et al., 2022).

Consumer-grade and recycled PE and PP samples were included as they contain common fillers (talc and calcium carbonate) or stabilisers (Irganox), and this study sought to investigate whether these additives would deactivate or hinder the catalyst system.

A decrease in MFI was observed when comparing the virgin polymers to the recycled samples. The increased melt elasticity of the recycled samples is attributed to crosslinking and chain branching of the polymer's molecular structure induced by the hot melt extrusion step they underwent. In contrast to this, the consumer-grade polymers have comparable MFIs to the virgin polymers, with the slight differences likely being a result of the difference in molecular weight between the virgin and consumer-grade samples.

4.2 Catalyst characterisation

4.2.1 X-ray Diffraction (XRD) and X-ray fluorescence (XRF) analysis

The resulting XRD pattern from the XRD analysis of the metathesis catalyst (WO_x/SiO_2) is depicted in Figure 4-1.

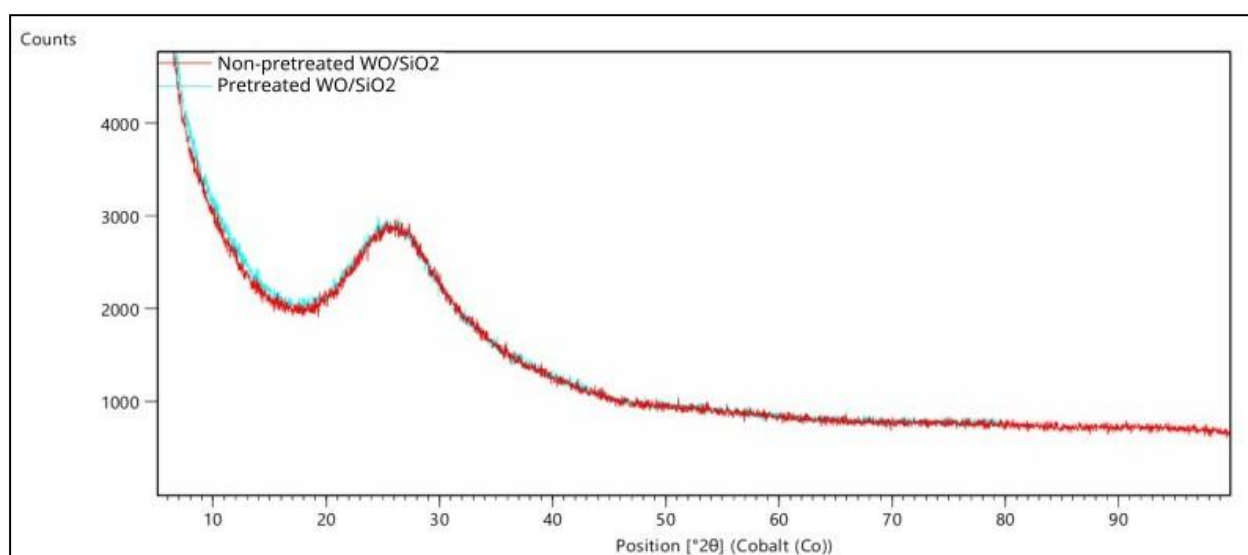


Figure 4-1: XRD pattern of non-pretreated (red) and pretreated (blue) WO_x/SiO_2

Figure 4-1 exhibits a broad peak centred around $20\text{--}30^\circ$ 2θ , which was expected and characteristic of amorphous silica (SiO_2). Furthermore, no distinct diffraction peaks corresponding to tungsten or tungsten oxide were observed, although Energy Dispersive X-ray Spectroscopy (EDS) confirmed its presence on the silica surface. This suggests that tungsten is highly dispersed on the silica surface. Finally, when comparing the diffraction patterns of pretreated vs non-pretreated samples, no noticeable shifts, additional peaks, or significant changes in peak intensity were observed, suggesting that pretreatment did not alter the structure of the WO_x/SiO_2 catalyst.

The resulting XRD pattern from the XRD analysis of the dehydrogenation catalyst ($\text{Pd}/\gamma\text{-Al}_2\text{O}_3$) is depicted in Figure 4-2.

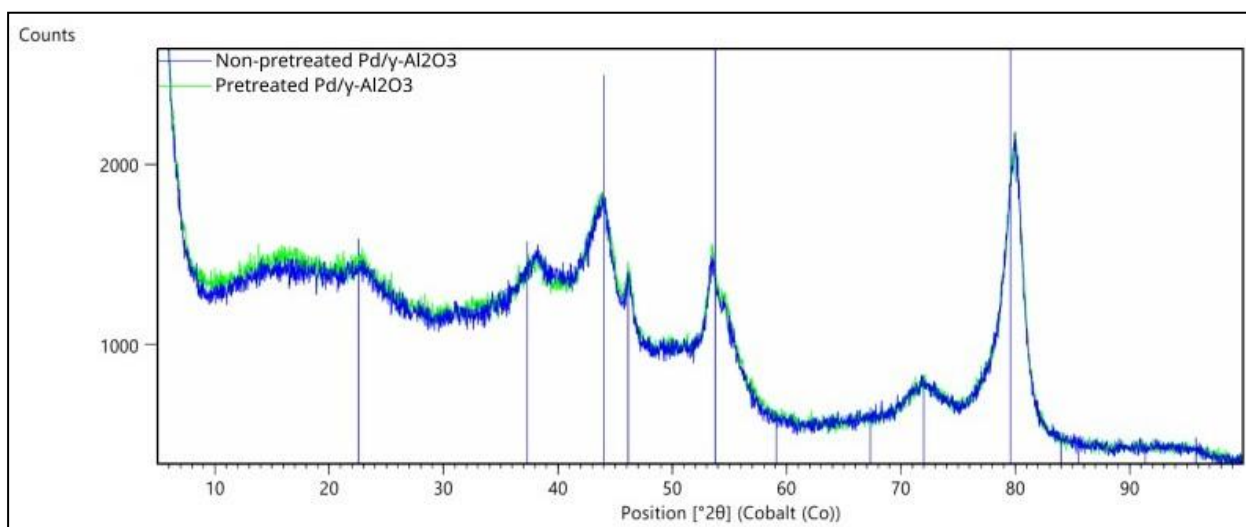


Figure 4-2: XRD pattern of non-pretreated (blue) and pretreated (green) Pd/ γ -Al₂O₃

Figure 4-2 exhibited peaks that match crystalline γ -Al₂O₃ with nanosized crystallites. This indicates an alumina support with a high surface area. Furthermore, no distinct peaks corresponding to palladium or palladium oxide were observed, indicating that palladium was highly dispersed on the alumina support and existed as nanoparticles. Finally, it was found that the XRD patterns of pretreated and non-pretreated Pd/ γ -Al₂O₃ were nearly identical, which means that the pretreatment step did not affect the crystallinity of the γ -Al₂O₃ support, nor did it induce sintering or crystallisation of Pd into larger particles. As observed with the WO_x/SiO₂ samples, the pretreatment step did not induce any structural changes in the Pd/ γ -Al₂O₃ samples.

Additionally, the XRF analysis also confirmed the chemical stability of both the WO_x/SiO₂ and Pd/ γ -Al₂O₃ samples before and after pretreatment, as no significant changes in elemental composition were observed.

4.2.2 N₂ low-pressure adsorption analysis

The BET surface area of the WO_x/SiO₂ catalyst was found to be 464 m²/g and the BJH desorption pore diameter and cumulative pore volume to be 6.60 nm and 0.78 cm³/g, respectively. Resultantly, the WO_x/SiO₂ catalyst can be classified as a mesoporous material. Additionally, a N₂ adsorption-desorption isotherm could be constructed for pretreated WO_x/SiO₂, which is illustrated in Figure 4-3.

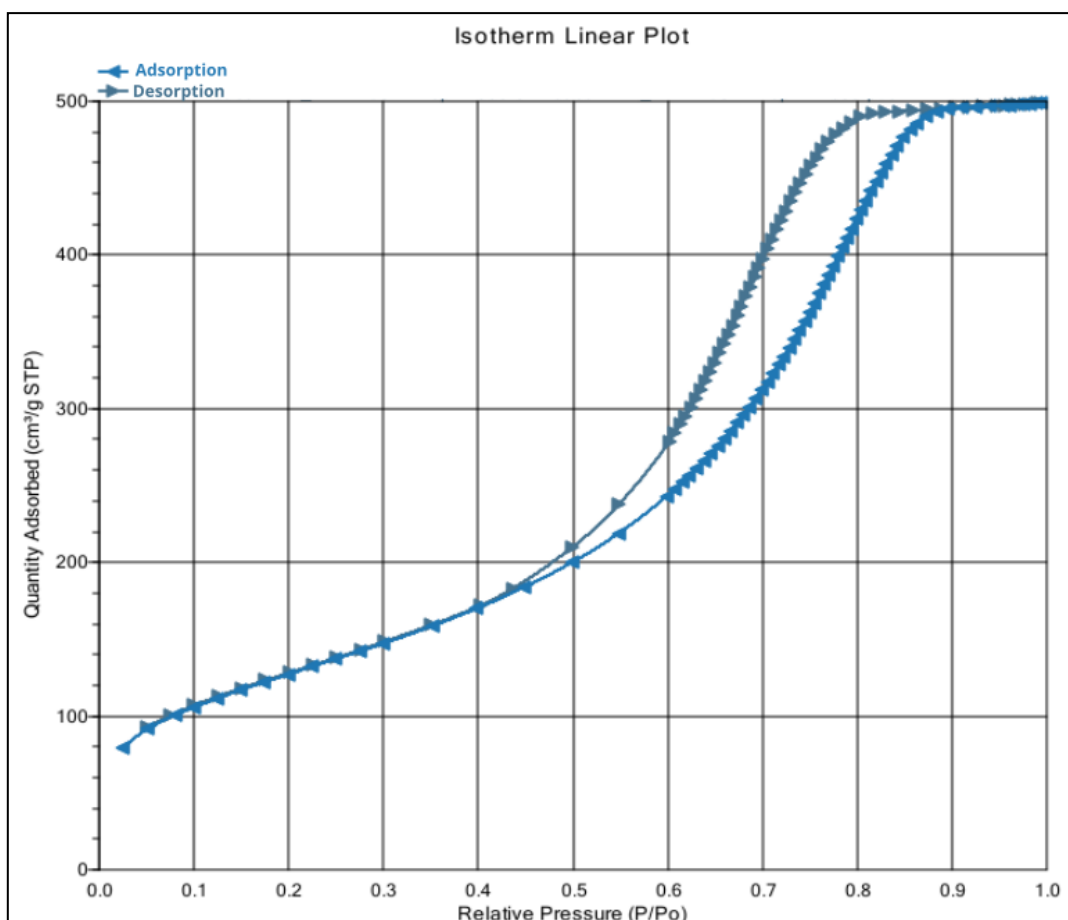


Figure 4-3: N₂ adsorption-desorption isotherm of WO_x/SiO₂

From the steep desorption branch of Figure 4-3, it can be deduced that the catalyst consists mostly of ink-bottle pores (narrow pore openings with wider internal cavities). Also, the hysteresis loop (difference between the adsorption and desorption branches) can be classified as an H2-type hysteresis with some features of H3, indicating that the catalyst has a complex and interconnected pore structure.

For the Pd/γ-Al₂O₃ catalyst, the BET surface area was calculated to be 103 m²/g with a BJH desorption pore diameter and cumulative pore volume of 7.60 nm and 0.25 cm³/g, respectively. The large difference in surface area between the WO_x/SiO₂ and Pd/γ-Al₂O₃ catalysts can be attributed to the WO_x/SiO₂ being a powder with an average particle size of approximately 120 μm, whilst the Pd/γ-Al₂O₃ was in pellet form, with each pellet having a diameter of roughly 3.2 mm.

A N₂ adsorption-desorption isotherm could also be constructed for pretreated Pd/γ-Al₂O₃ and is illustrated in Figure 4-4.

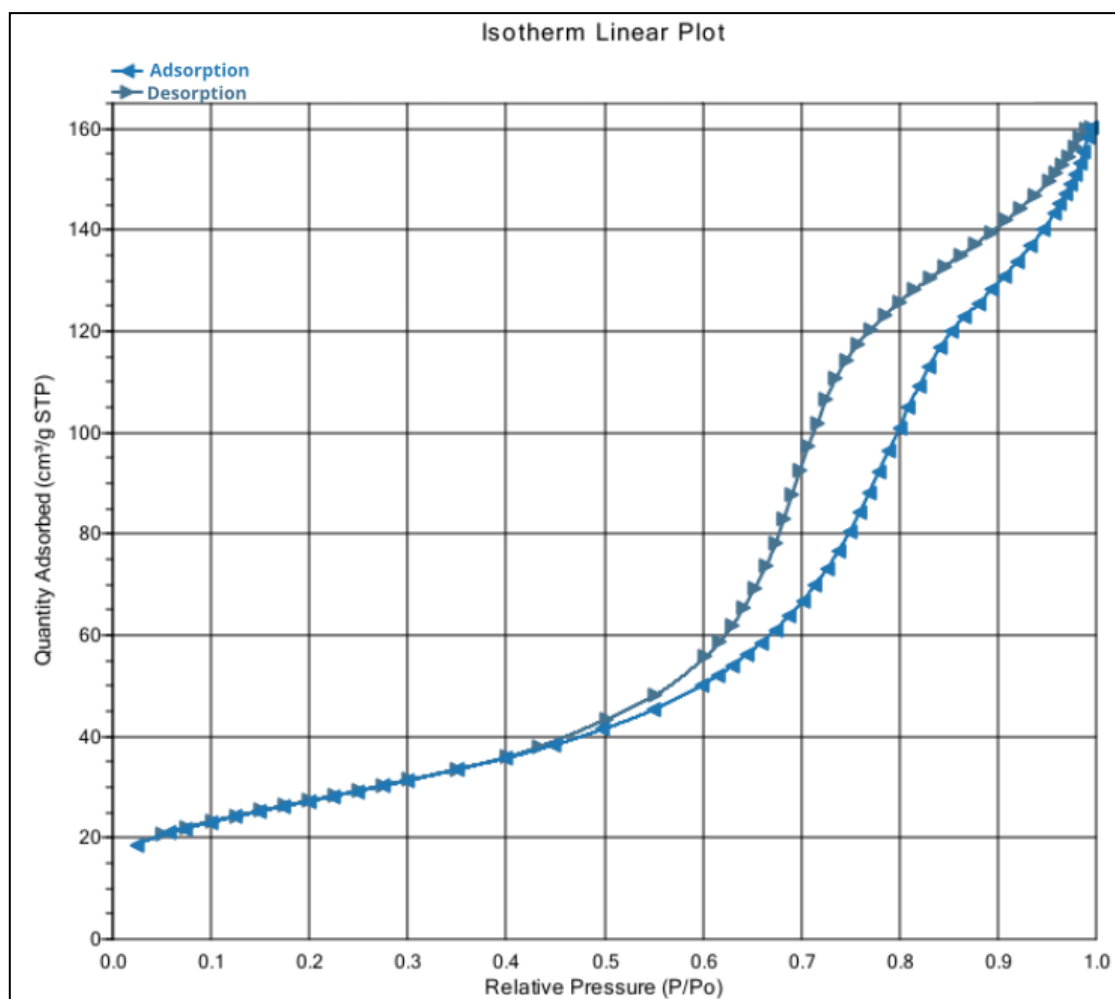


Figure 4-4: N₂ adsorption-desorption isotherm of Pd/γ-Al₂O₃

The pore diameter and structure of the two catalysts were highly comparable, with the Pd/γ-Al₂O₃ also having mesopores with an ink-bottle shape, as indicated by the adsorption-desorption isotherm in Figure 4-4. The cumulative pore volume of the Pd/γ-Al₂O₃ catalyst was less than that of the WO_x/SiO₂ catalyst, indicating a slightly less intricate pore structure; this observation is supported by the hysteresis loop, which is a good example of a strict H2-type hysteresis.

Lastly, there was no change observed in surface area, pore diameter, or cumulative pore volume for either the WO_x/SiO₂ or Pd/γ-Al₂O₃ catalysts when comparing pretreated to non-pretreated samples.

4.2.3 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS)

Figures 4-5 and 4-6 show SEM images of the WO_x/SiO₂ and Pd/γ-Al₂O₃ catalysts, respectively, illustrating the surface structure and approximate size distribution of the catalyst samples.

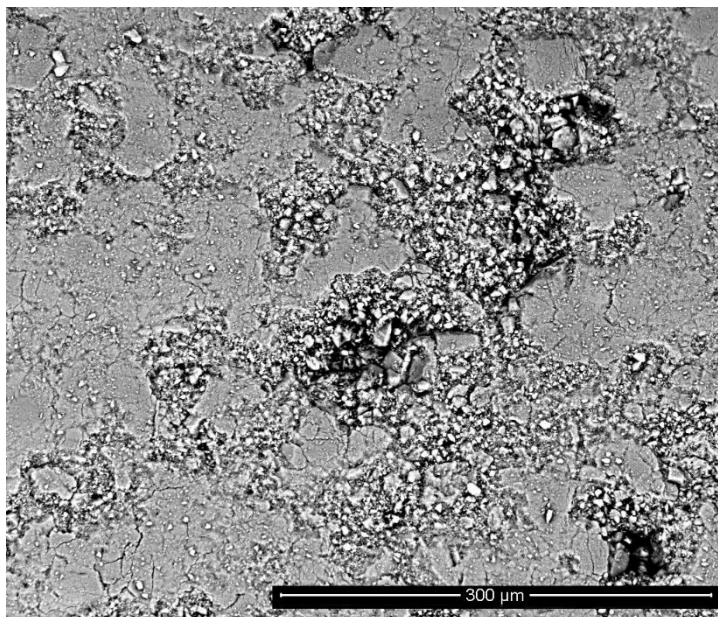


Figure 4-6: SEM image of Pd/γ-Al₂O₃ (dehydrogenation catalyst)

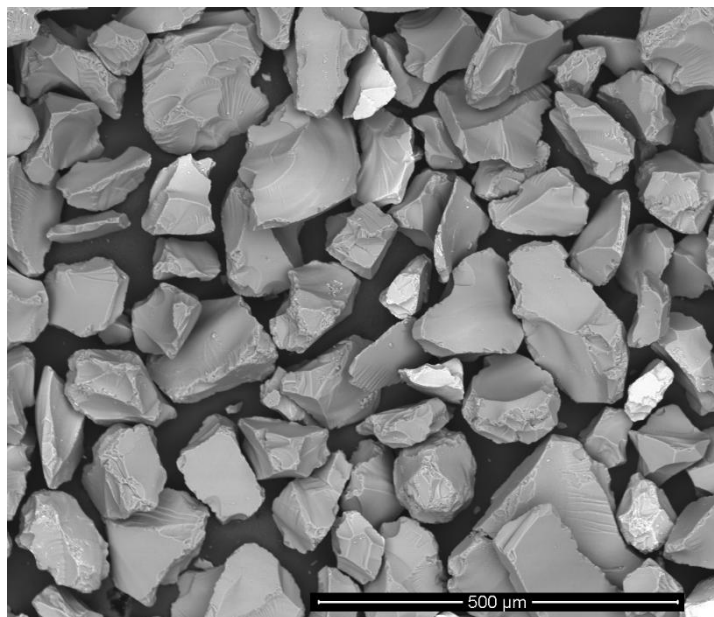


Figure 4-5: SEM image of WO_x/SiO₂ (metathesis catalyst)

The WO_x/SiO₂ catalyst had flat surfaces and a broad particle size distribution, ranging from approximately 60 to 210 μm. The Pd/γ-Al₂O₃ catalyst was obtained as 3.2 mm pellets with a porous surface. Additionally, no change in surface morphology was detected between the pretreated and non-pretreated catalysts for both the WO_x/SiO₂ and Pd/γ-Al₂O₃ samples.

The EDS measurements showed that the surface loading of W on the metathesis catalyst was 1.8 wt.%, which is ideal as it minimises waste metal when synthesising the catalyst. Furthermore, this is very comparable to the loading ratio used by Kim et al. (2022), who employed a similar metathesis catalyst. The surface loading of Pd for the dehydrogenation catalyst was found to be 1.4 wt.%, which is higher than the overall loading of 0.5 wt.% for the entire pellet as reported by the manufacturer. This is good as it indicates that the active sites are more concentrated on the catalyst surface and, as a result, reaction rates will be less influenced by diffusion limitations. On the other hand, this Pd loading ratio is slightly lower than the Pt loading ratios reported by Kim et al. (2022) and Ellis et al. (2021) used for their dehydrogenation catalysts. However, as pointed out by the work of Moore (2024), the activity of Pd is nearly 4 times that of Pt in these types of applications, and thus the Pd/γ-Al₂O₃ catalyst should perform as good if not better than the Pt alternatives. Lastly, EDS also revealed that there was no difference in the metal loading ratios between the pretreated and non-pretreated samples for either of the catalysts.

4.3 Initial catalyst system testing and control experiments

Given that no previous work detailing the use of WO_x/SiO₂ along with Pd/γ-Al₂O₃ for the TDOCM of PE and n-decane exists, initial experiments sought to determine if the catalyst pairing did

indeed have a catalytic effect on the reaction. To this end, the reactor was loaded with virgin HDPE and n-decane at a 1:10 weight ratio with a 5:1 plastic-to-catalyst weight ratio. The experiment was performed at 300°C for 3 hours. As illustrated by Table 4-2, the liquid fraction recovered was found to contain only alkanes, with no aromatics or alkenes detected and compounds as large as C₂₈ were confidently identified. Furthermore, the FTIR spectra of this liquid fraction show only the presence of saturated bonds (Appendix C, Figure C-1). Additionally, a mass decrease of nearly 20% was also observed when comparing the initial mass of HDPE inserted to the mass of solids recovered.

Table 4-2: Summary of compounds in the liquid fraction detected by GC-MS analysis

Retention time (min)	Compound name
15.83	3-ethyl-3-methyldecane
16.03	4-methyldodecane
16.75	Tridecane
17.63	9-methylnonadecane
18.44	Tetradecane
19.24	3,5-Dimethyldodecane
20.02	Pentadecane
20.74	7-methylpentadecane
21.52	Hexadecane
22.93	Heptadecane
23.52	9-methylheptadecane
24.28	Octadecane
25.56	Nonadecane
26.78	Eicosane
27.95	Heneicosane
29.07	4-methylnonadecane
30.14	2-methylhexadecane
31.17	Tetracosane
32.17	Pentacosane
34.04	9-octyleicosane

In contrast, two control runs were performed under the same conditions, omitting either the metathesis catalyst (WO_x/SiO₂) or the dehydrogenation catalyst (Pd/γ-Al₂O₃) in each case. These experiments showed no decrease in mass between the starting polymer and the recovered solids. Additionally, the largest compound identified in the liquid fraction was only C₁₈ (Figure 4-7(B)); this strongly suggests that the catalyst pairing succeeds in catalysing the dehydrogenation and olefin cross-metathesis of n-decane and virgin polyethylene. One might have expected that the control run with only Pd/γ-Al₂O₃ present would at least lead to some unsaturated hydrocarbons present in the products; however, as Ellis et al. (2021) also found, this was not the case. The reason for this is that once conditions allow for endothermic dehydrogenation reactions to occur, the exothermic hydrogenation reactions will occur at an equal rate to produce more stable

saturated compounds. This shows how the metathesis reaction consumed the products of the dehydrogenation step to “pull” reactants through a thermodynamically limited reaction step. However, the experimental run with only Pd/γ-Al₂O₃ produced slightly more H₂ than the experimental run with only WO_x/SiO₂, which is expected and stems from liberated hydrogen that volatilises to the gas phase instead of remaining in the intermediate pool. This is also a good indicator that Pd/γ-Al₂O₃ catalyses the dehydrogenation step.

Lastly, to confirm that cross-incorporation between PE and n-decane was occurring in these reactions, a final control experiment was performed under the same conditions with both catalysts present, but without any virgin HDPE present in the reactor. Again, only alkanes were identified in the recovered liquid; however, no compounds larger than C₁₆ were identified, meaning all larger components identified in the first experiment originated from the cross-incorporation between virgin HDPE and n-decane. Figure 4-7 depicts the C₁₃ to C₂₇ sections of chromatograms derived from GC-MS analysis of the liquid fractions recovered from virgin HDPE- and control TDOCM experiments; additionally, an n-decane blank (Figure 4-7 (D)) is also added for reference.

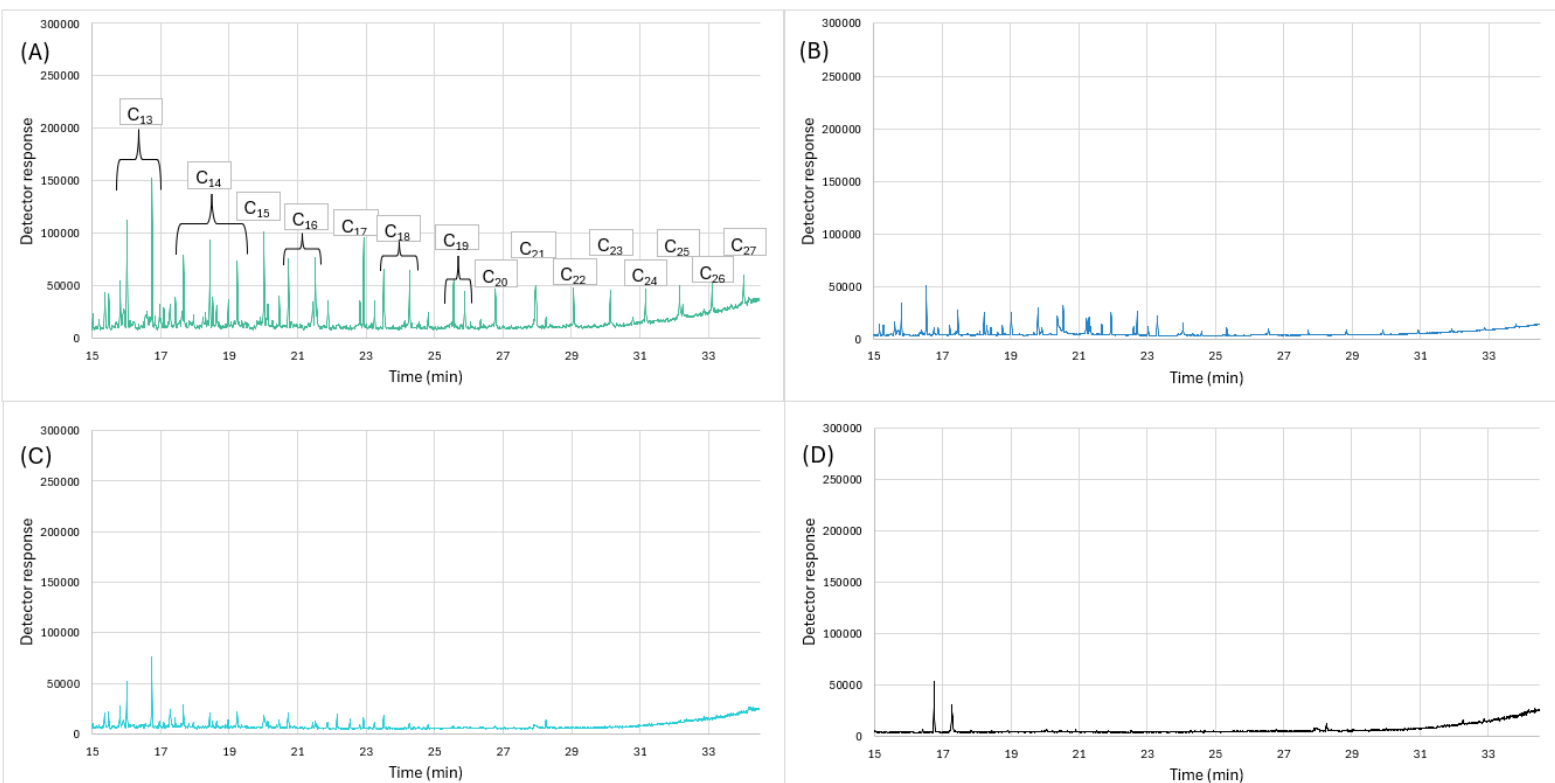


Figure 4-7: Chromatograms derived from GC-MS analysis of liquid fractions recovered for TDOCM control experiments with (A) virgin HDPE with all catalysts present, (B) virgin HDPE with WO_x/SiO₂ absent, (C) all catalysts present but virgin HDPE absent, and (D) an n-decane blank added for reference.

These initial results are quite promising as similar polymer weight reductions and product distributions were obtained by Jia et al. (2016) and Ellis et al. (2022) with their catalyst systems

of (^t-BuPOCOP)Ir and Re₃O₇/γ-Al₂O₃ or SnPt/γ-Al₂O₃ and Re₃O₇/γ-Al₂O₃, respectively. However, they were limited to a maximum reaction temperature of 200 °C due to the thermal stability constraints of the Re₃O₇/γ-Al₂O₃ catalyst and could only obtain those results for experimental times of 15 to 72 hours. The increased thermal stability of the WO_x/SiO₂ catalyst synthesised in this study enabled reaction temperatures of 300 °C, thereby decreasing required reaction times to only 3 hours.

Furthermore, this increased reaction temperature meant that the catalyst loading ratio used in this study was nearly 25 times lower than the loading ratios used by Jia et al. (2016) and Ellis et al. (2022). The Pd/γ-Al₂O₃ dehydrogenation catalyst used in this study also showed excellent reactivity when compared to the findings of Kim et al. (2022), who also used WO_x/SiO₂ at 300 °C but instead opted for Pt/γ-Al₂O₃ (1 wt.% loading) as their dehydrogenation catalyst. The catalyst loading ratios used in this work were half that implemented by Kim et al. (2022) to obtain similar results. Consequently, the tandem catalyst system comprising Pd/γ-Al₂O₃ and WO_x/SiO₂ represents significant progress toward reducing the reliance on costly catalysts for the effective degradation of polyethylene (PE) via tandem dehydrogenation–olefin metathesis (TDOCM), thereby enhancing the economic feasibility of TDOCM as a chemical recycling strategy.

4.4 Applicability of the catalyst system on other polyolefins

After establishing that WO_x/SiO₂ and Pd/γ-Al₂O₃ could be used to successfully degrade virgin HDPE, it was necessary to determine whether factors such as the linearity of the PE sample or the presence of additives (plasticisers, stabilisers, and antioxidants) in the polymer would in any way affect the effectiveness of the catalysts or the reaction scheme and also how this would manifest itself in the distribution and quality of the products. To this end, the experimental runs detailed in Table 4-3 were performed.

Table 4-3: Reaction parameters and yields of experimental runs relating to Section 4.4

Run nr.	Polymer ID*	Reaction time (hr)	Initial reaction pressure (bar)	Catalyst:Polymer ratio (g:g)	Polymer:Decane ratio (g:g)	Product yields (wt. %)		
						Wax (±1.1)	Oil (±4)	Gas (±0.9)
1	HDPE_V	3	5	1:5	1:10	31	66.5	2.5
2	LDPE_V	3	5	1:5	1:10	20.6	71.2	8.2
3	PE_C	5	15	1:5	1:10	0	82.4	17.6
4	PE_R	3	5	1:5	1:10	21.6	76.9	1.5
5	PP_V	3	5	1:5	1:10	0	80.8	19.2

*(_V): Virgin sample, (_C): commercial grade, (_R): recycled sample

Given that LDPE has a more branched structure than HDPE, there was a possibility that this non-linearity would lead to a less significant decrease in molecular weight of the starting polymer due to the dehydrogenation catalyst targeting C-H bonds on side chains rather than the main carbon

backbone. Furthermore, there is a possibility that the branched nature of LDPE could lead to relatively more iso-alkanes being formed when compared to the degradation of HDPE. To investigate this, the reactor was loaded with virgin LDPE and n-decane, again at a 1:10 weight ratio and a 5:1 plastic-to-catalyst weight ratio, heated to 300°C, and maintained for 3 hours (Run 2 vs. Run 1 in Table 4-3). The FTIR spectra of the liquid product derived from the experiment utilising virgin LDPE is depicted in Figure 4-8.

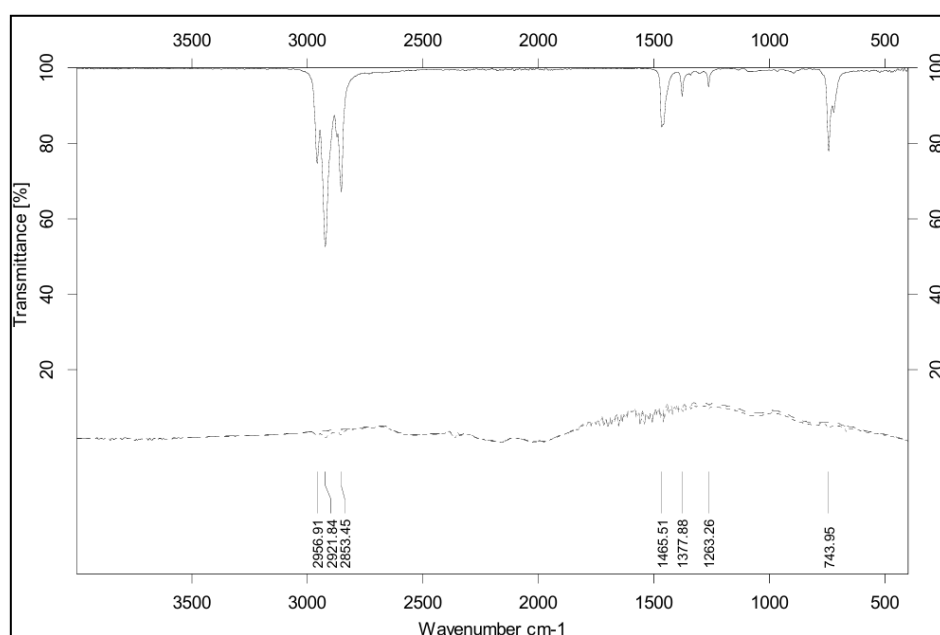


Figure 4-8: FTIR spectra of the liquid fraction produced when using virgin LDPE

Using virgin LDPE resulted in a higher conversion compared to virgin HDPE, with the recovered solids showing a nearly 40% decrease in weight compared to the initial amount of polymer inserted. This is attributed to the difference in starting molecular weight of the HDPE vs LDPE, being 165,000 g/mol and 30,000 g/mol, respectively. Additionally, the recovered liquid fraction again only consisted of alkanes, as confirmed by the FTIR spectra in Figure 4-8. Furthermore, upon investigation of the chromatograms of the two samples, there was no preference towards iso-alkane production identified when comparing the oils derived from LDPE to those derived from HDPE, with the LDPE-derived liquid basically containing the exact same compounds as identified in Table 4-3. Likewise, the compositions of the gas fractions derived from the two runs were very similar, as depicted in Figure 4-9.

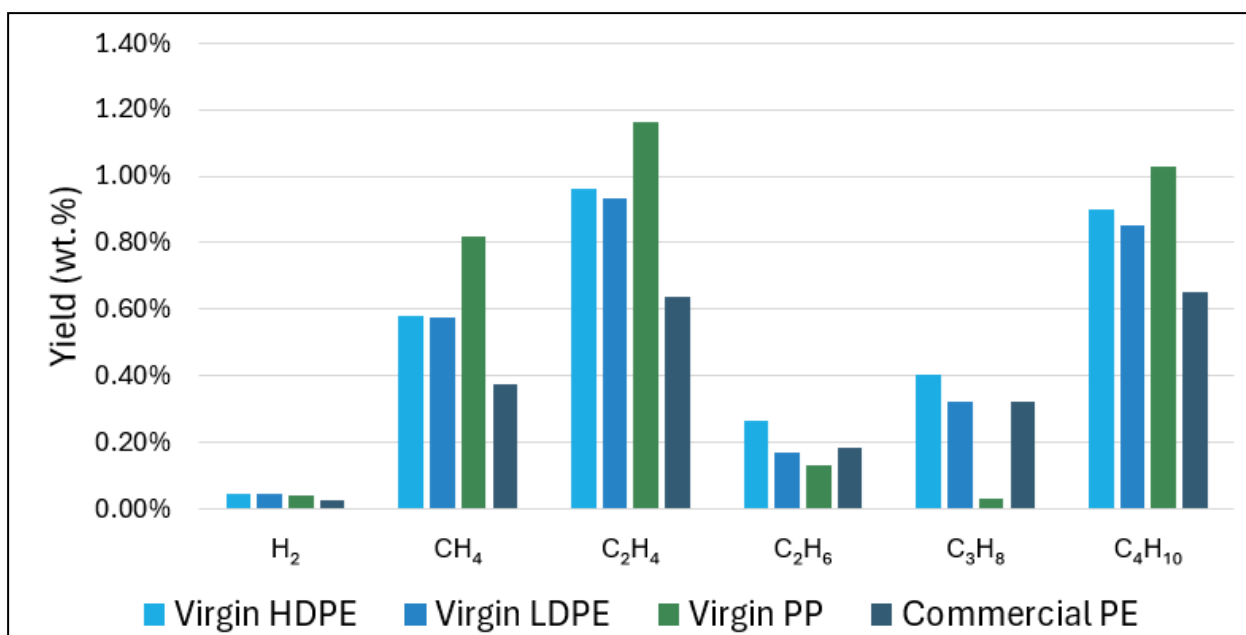


Figure 4-9: Composition of the gas fractions derived from TDOCM of virgin LDPE, virgin HDPE, commercial PE or virgin PP with n-decane

Thus, it can be concluded that the performance of the catalyst system is mostly unaffected by the linearity of the PE sample. Similarly, Jia et al. (2016) also found that the structure of the parent PE sample had little effect on the product distributions; however, they achieved this with a more expensive Ir-based dehydrogenation catalyst. Additionally, these results are promising because it means if the system were to be expanded to a real-world recycling scheme, there would be no need to sort and separate different types of PE.

Expanding on this goal, if this TDOCM catalyst system is to one day be developed to a full-scale chemical recycling scheme, it would also need to be compatible with the additives found in commercial-grade polyolefins. To test the compatibility of the catalyst system with common commercial additives (e.g., plasticisers, stabilisers, and antioxidants) a commercial-grade polyethylene sample (obtained from a local recycling plant) that also underwent a hot melt extrusion recycling step was inserted into the reactor and the TDOCM experiment was conducted at the same conditions as the aforementioned experiments (Run 4 from Table 4-3).

The commercial-grade PE sample showed a mass decrease of roughly 25%, which is similar to the decrease the virgin HDPE sample underwent. As with the virgin samples (Runs 1 and 2), the liquid fraction derived from the commercial-grade PE sample contained only alkanes, with compounds up to C₂₉ being identified. Furthermore, the overall composition of the liquid and gas fraction was very similar to those derived from virgin PE samples, with no selectivity difference towards n- or iso-alkanes identified. Thus, it is concluded that the presence of additives does not

affect the quality of the products derived, nor does it dampen the effectiveness of the TDOCM catalyst system in degrading the polymer sample.

Given the robustness of the TDOCM catalyst system thus far, the scope of tested polyolefins was further expanded to include polypropylene (PP), which has not yet been reported in the literature. A virgin PP sample ($M_w = 250\,000$ g/mol, PDI = 3.73) was subjected to TDOCM at 300 °C for 3 hours, with a 1:10 Polymer to n-decane weight ratio and a 5:1 polymer to WO_x/SiO_2 weight ratio (Run 5 from Table 4-3). The catalyst system once again proved to be very effective in degrading polyolefins under mild conditions, as the entire virgin PP sample was converted to either liquid (81 ± 4 wt.%) or gas (19 ± 0.9 wt.%). The GC-MS chromatogram of the liquid product derived from this experiment is depicted in Figure 4-10 (A) along with the chromatogram of the liquid product from virgin LDPE experiments (Figure 4-10(B)) for comparison.

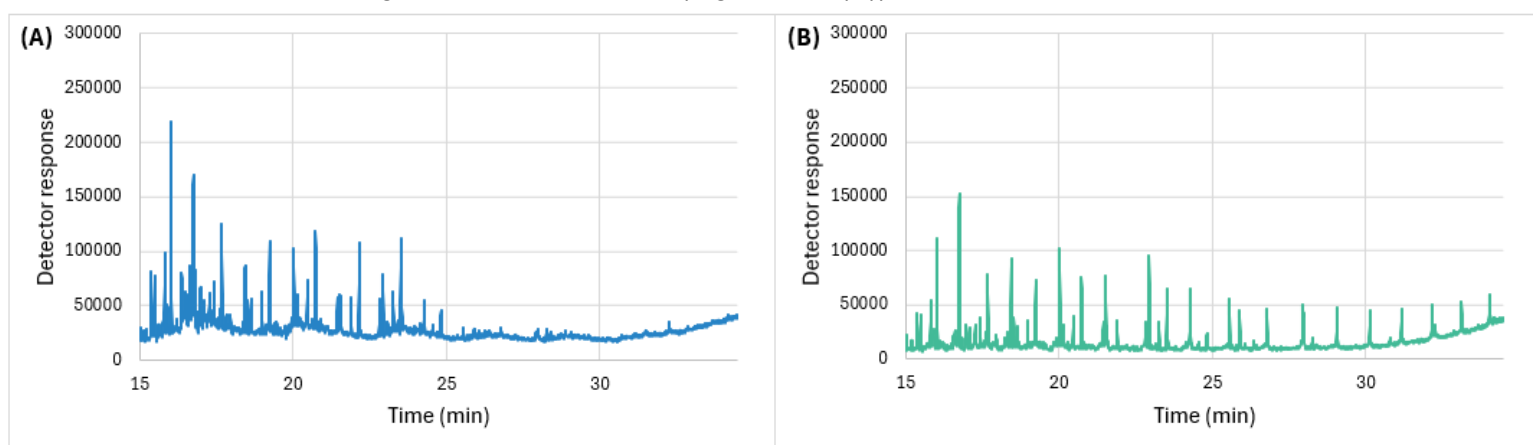


Figure 4-10: GC-MS chromatograms of liquids derived from TDOCM of (A) virgin PP and (B) virgin LDPE

Analysis of the liquid fraction identified only alkanes ranging from C_8 to C_{18} , which are considerably lighter than the PE-derived oils, indicating a higher reaction rate. Furthermore, upon comparing the composition of virgin PP-derived oils to that of virgin PE-derived oils, a clear preference for iso-alkane formation was observed with the PP sample. This observation is expected and easily explicable with the help of the TDOCM mechanism of PP and n-decane depicted in Figure 4-11.

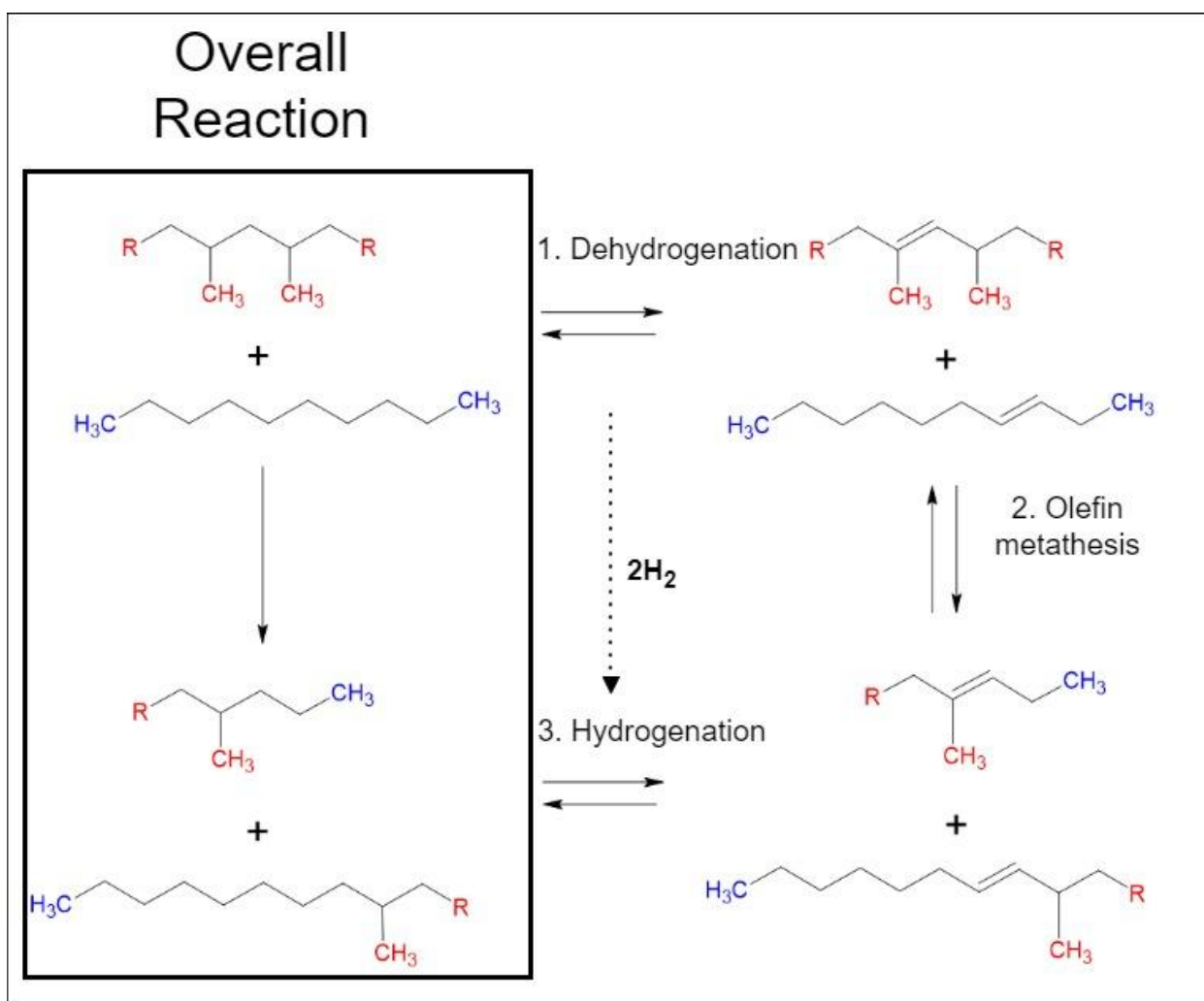


Figure 4-11: Proposed reaction scheme for the TDOCM of PP and n-decane

As seen in Figure 4-11, the dehydrogenation step will most likely liberate hydrogens from the C–C backbone (secondary and tertiary C–H bonds), rather than hydrogen atoms from the methyl radicals (primary C–H bonds) as the bond dissociation energies (BDE) for secondary and tertiary C–H bonds range from 392–400 kJ/mol which is lower and relatively easier to break than the BDEs of primary C–H bonds at 410 kJ/mol (Huang et al., 2018). As a result, after olefin cross-metathesis and hydrogenation occur, the shortened PP chain retains all initial methyl groups. It is important to remember that this is a continuous process performed in large excess of n-decane, thus the primary products can again undergo TDOCM, which eventually leads to the considerable decrease in M_w observed in the starting polymer sample.

4.5 Controlling the product distribution and composition

Another significant gap in the literature covering TDOCM is a thorough understanding of how different reaction parameters, such as catalyst loading ratios, light alkane to polymer ratios, and reaction pressure, affect the quality and distribution of products derived from TDOCM. Table 4-4

summarises the reaction parameters and product yields of the TDOCM experiments most relevant to Section 4.5.

Table 4-4: Reaction parameters and yields of experimental runs relating to Section 4.5

Run nr.	Polymer ID*	Reaction time (hr)	Initial reaction pressure (bar)	Catalyst:Polymer ratio (g:g)	Polymer:Decane ratio (g:g)	Product yields (wt. %)		
						Wax (± 1.1)	Oil (± 4)	Gas (± 0.9)
6	HDPE_V	3	5	1:5	1:5	48.0	39.3	12.7
7	LDPE_V	3	5	1:5	1:5	26.1	45.7	28.2
8	PP_V	3	5	1:5	1:5	0	62.4	37.6
9	LDPE_V	3	7.5	1:5	1:10	20.0	68.6	11.4
10	LDPE_V	3	15	1:5	1:10	15.4	83.8	0.8
11	PP_V	3	15	1:5	1:5	0	72.0	28.0
12	PP_V	1	5	1:5	1:10	17.5	68.4	14.1
13	HDPE_V	3	5	1:2	1:10	9.3	65.2	25.5
14	LDPE_V	3	5	1:2	1:10	9.4	67.4	23.2
15	PP_V	3	5	1:2	1:10	0	76.0	24.0
16	PP_C	5	15	1:5	1:10	0	78.5	21.5

*(_V): Virgin sample, (_C): consumer grade, (_R): recycled sample

4.5.1 Influences of light alkane-to-polymer loading ratios

To investigate the effects of light alkane to polymer ratio, TDOCM reactions were performed on virgin HDPE, LDPE and PP at 300 °C for 3 hours, with a 1:5 catalyst-to-polymer ratio, and varying the polymer-to-n-decane weight ratio from 1:10 to 1:5.

For virgin HDPE a significant increase in the wax fraction from 31 wt.% to 48 wt.% was observed as seen in Figure 4-12(A), when reducing the n-decane to polymer weight ratio from 10:1 to 5:1. A similar observation was made by Jia et al. (2016) where they investigated the TDOCM of virgin PE and n-octane using variations of Ir-based dehydrogenation catalysts to investigate the location of the double bonds induced in their PE samples. The increased wax yield is likely due to a lack of excess light alkane, which resulted in an increase in redundant metathesis reactions between PE chains, which would not lead to the effective breakdown of the PE sample. A significant increase in the gas yield was also observed, as shown in Figure 4-12(B), which further supports the argument that reducing the amount of n-decane results in an increase in the amount of redundant metathesis reactions between PE chains. These lighter alkanes ($<C_5$) possibly originate from double bonds induced close to the ends of PE chains, which, after a metathesis reaction, would form either very small or very large alkanes, which coincides with the product distribution obtained. Variations in dehydrogenation catalyst type or structure can alter the degree of favour toward terminal dehydrogenation, as highlighted by the work of Jia et al. (2016) and Haibach et al. (2012).

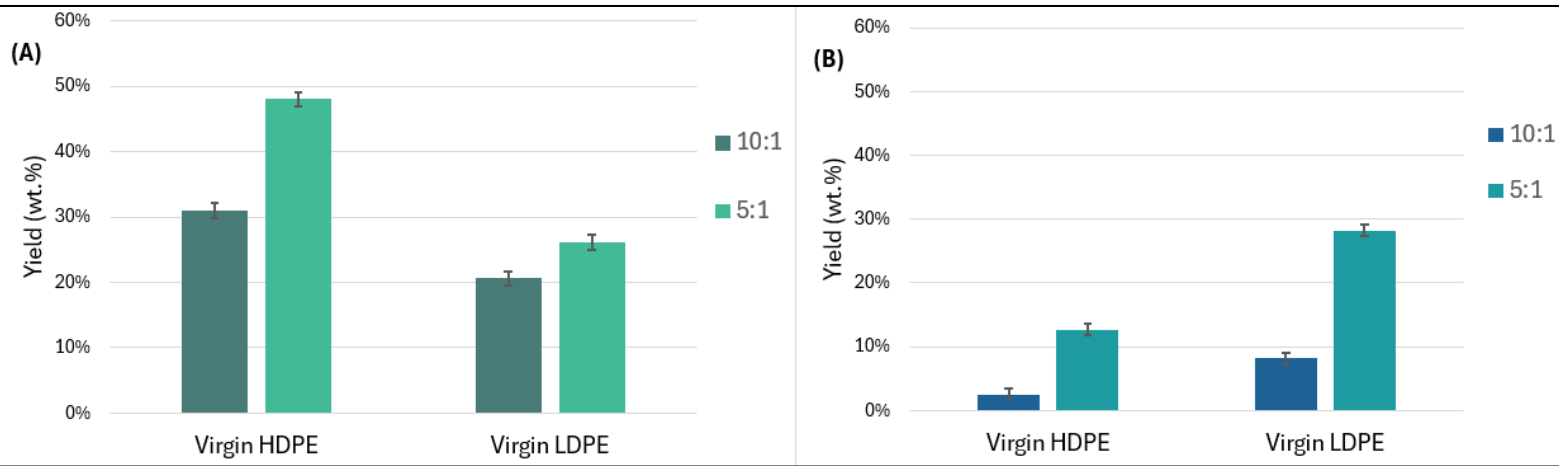


Figure 4-13: Influence of n-decane to polymer weight ratio (10:1 vs. 5:1) on the (A) wax yield and (B) gas yield obtained from TDOCM experiments performed either virgin HDPE or LDPE

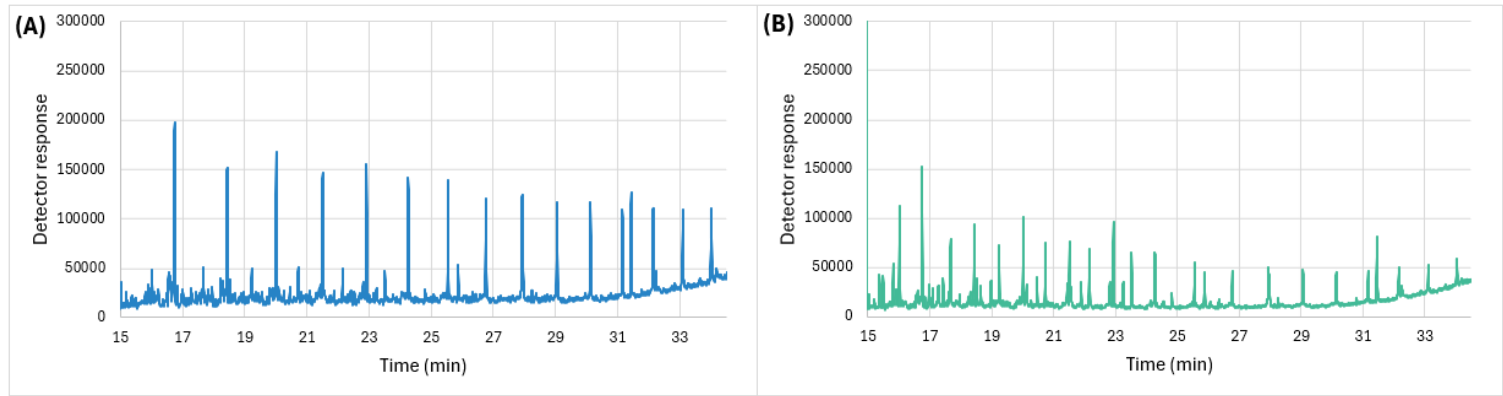


Figure 4-12: C₁₃ to C₂₈ range of GC-MS chromatogram of the oils derived from TDOCM with virgin HDPE and a polymer-to-n-decane weight ratio of (A) 1:5 and (B) 1:10

The chromatograms derived from GC-MS analysis of the liquid fraction (Figure 4-13) also show a significant skew towards the heavier compounds (>C₁₃) for the oils derived from TDOCM experiments performed at a n-decane to PE weight ratio of 5:1. This highlights the necessity of excess light alkanes in TDOCM reactions to effectively break down the polymer structure by reducing the possibility of metathesis between two PE chains.

When performing the same experiments on virgin LDPE the same trend of increased wax yield was observed, from 20.5 wt.% to 26 wt.%, when decreasing the n-decane to polymer weight ratio from 10:1 to 5:1. Additionally, the liquid fraction also indicates a noticeable shift towards heavier compounds when compared to the 10:1 run. This again indicates the occurrence of redundant metathesis reactions between PE chains instead of cross-metathesis between PE chains and decene due to lack of excess decane. However, the increase in wax production was not as pronounced with the virgin LDPE sample as with the virgin HDPE sample. This can be attributed

to two likely factors. Firstly, the branched or non-linear nature of LDPE compared to HDPE, as illustrated by Figure 4-14.

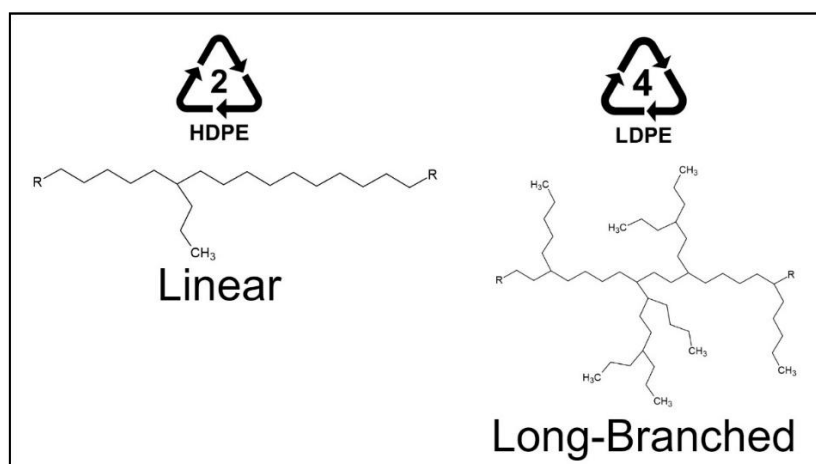


Figure 4-14: Linear structure of HDPE compared to the branched structure of LDPE

For LDPE, when a metathesis reaction involving a branched chain (comparable in size to n-decane) of the polymer occurs, it can still lead to significant polymer degradation. Secondly, as illustrated by Moore et al (2025), it is likely that the LDPE is more soluble in n-decane at the given reaction temperatures due to its relatively higher MFI (32 g/10min for virgin LDPE vs 14 g/10min for virgin HDPE). As a result, LDPE requires a light alkane in a smaller excess than HDPE to achieve substantial degradation of the starting polymer.

However, LDPE exhibited the same tendency as HDPE to produce a larger gas fraction when the amount of n-decane present in the reactor was reduced. This is again attributed to double bonds induced near the ends of polymer chains, which would result in very light alkanes to form if two terminally unsaturated PE molecules participated in a metathesis reaction. Additional contributors to the increased gas production with both the virgin LDPE and HDPE experiments could be the occurrence of catalytic cracking of the PE chains due to a lack of decene molecules to stabilise them and incorporate with; this is evident by the increased hydrogen content of gases derived from the 1:5 experimental runs as depicted by Figure 4-15. The n-decane also acts as a heat sink and diluent for the reaction; thus, the decreased n-decane concentration leads to reduced hydrogen solubility and dispersion, which results in unsaturated fragments exiting to the gas phase rather than further partaking in cross-metathesis and sequential hydrogenation. Moore et al. (2025) reached a similar conclusion, postulating that hydrogen accessibility directly influences the rate of alkane formation.

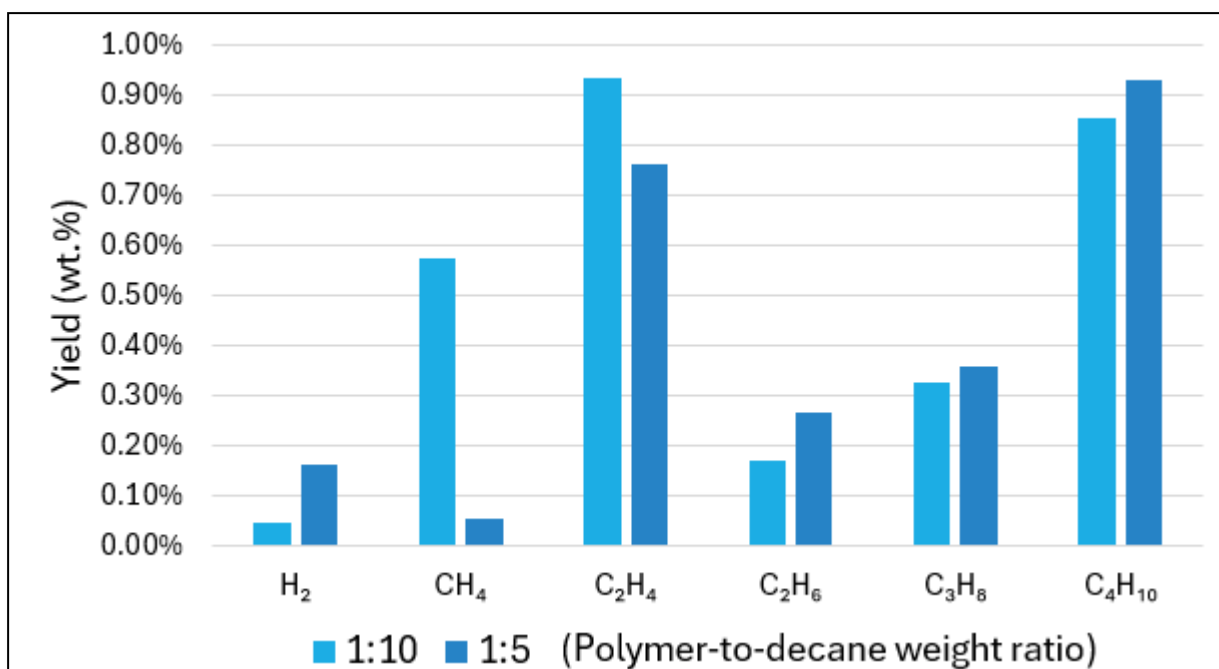


Figure 4-15: Composition of the gas fractions derived from TDOCM experiments performed on LDPE and n-decane at 300°C for 3 hours, with a 1:5 catalyst to polymer ratio at a 1:10 (Blue) or 1:5 (Orange) polymer-to-n-decane ratio

Finally, TDOCM experiments were also performed on virgin PP at 300 °C for 3 hours, using a 1:5 catalyst to polymer ratio, and PP to n-decane weight ratios of 1:10 and 1:5 (Run 5 vs. Run 8). The first observation was that decreasing the amount of n-decane relative to the amount of PP did not lead to an increase in the solid yields, as was the case with PE experiments. Rather, the entire virgin PP sample was degraded to only liquids and gases at both the 1:10 and 1:5 ratios. However, when decreasing the PP to n-decane weight ratio from 1:10 to 1:5, the gas yield increased from only 19 wt.% to nearly 38 wt.%. Furthermore, the liquid fraction also showed a significant decrease in the production of compounds larger than C₁₃. This is the inverse of the trend observed with PE samples and can be explained by the relatively weaker C–C backbone of PP due to the tertiary carbons. Because of these weaker bonds, the PP readily undergoes β-scission of the C–C bonds at the lower n-decane concentration, rather than the dehydrogenation, metathesis and hydrogenation sequence favoured at higher n-decane concentrations. These β-scission form short propyl radicals or allyl species, which rapidly escape to the gas phase, as the decreased decane content also results in a less viscous phase, leading to shorter retention times of small molecules. This argument is supported by the increase in hydrogen production noted in the gas product when decreasing the n-decane loading ratio, as depicted by Figure 4-16. From Figure 4-16, an increase in all the components is observed, due to the overall larger gas yield when decreasing the amount of n-decane; however, the increase in H₂ is disproportionately larger than the other components.

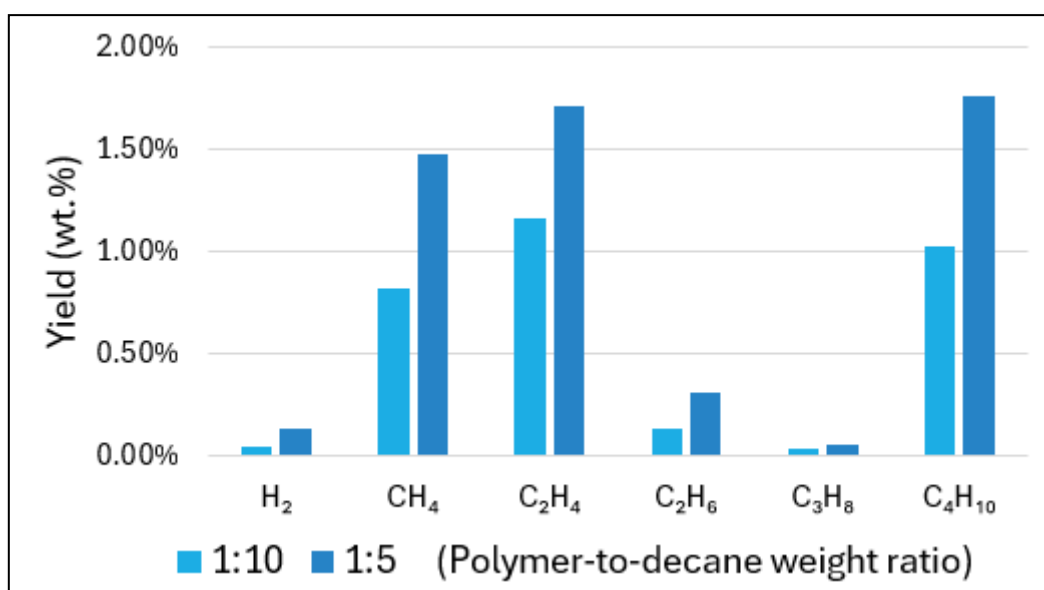


Figure 4-16: Comparison of the composition gas fractions obtained from TDOCM of virgin PP and n-decane for 1:10 vs. 1:5 polymer-to-n-decane weight ratio

Thus, the necessity of excess light alkanes in TDOCM to degrade polymer samples is evident. For PE, insufficient light alkanes result in an increase in the number of redundant metathesis reactions between two polymer chains, leading to significantly less effective breakdown of the polymer chains. When applying TDOCM to PP, a shortage of light alkanes favours the secondary reaction mechanism (β -scission of tertiary carbons), which yields much lighter, less valuable compounds than the TDOCM mechanism. Additionally, the role of the light alkane, not only as a co-reactant, but also as a moderator for heat transfer, hydrogen solubility, and retention of small molecules, was highlighted. It is concluded that for the catalyst pairing of WO_x/SiO_2 and $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$, at the reaction conditions investigated in this study, the lower limit for polymer to n-decane weight ratio is approximately 1:10 if effective degradation of PE and limited side reactions of PP are to be achieved.

4.5.2 Increasing the reaction pressure

It also quickly became apparent that reaction pressure could play a significant role in influencing product composition and distribution, as it directly affects factors such as the solubility of hydrogen and light compounds. To investigate the effects of reaction pressure on the system, TDOCM experiments were performed on virgin PP at 300 °C for 3 hours, with a 1:5 catalyst to polymer ratio, 1:5 polymer to n-decane ratio, and varying the initial pressure within the reactor from 5 bar to 15 bar, which resulted in maximum reaction pressures of 26 and 50 bar respectively (Run 8 vs. Run 11).

At both 5 and 15 bar initial pressure, the entire virgin PP samples were degraded to yield only liquid and gaseous products. Furthermore, as the pressure increased, the gas yield decreased by nearly 10 wt.% from 37.5 wt.% to 28 wt.%, suggesting that at elevated pressures the formation of larger compounds is favoured. The composition of the liquid fraction supports this argument: both experimental runs yielded only alkanes in the liquid phase, with the majority being smaller than C₁₅. However, there was a small shift towards slightly larger components observed in the liquid derived at higher pressures, as depicted by the marginally stronger response from compounds in the C₁₃ to C₂₀ range of the GC-MS chromatograms illustrated in Figure 4-17.

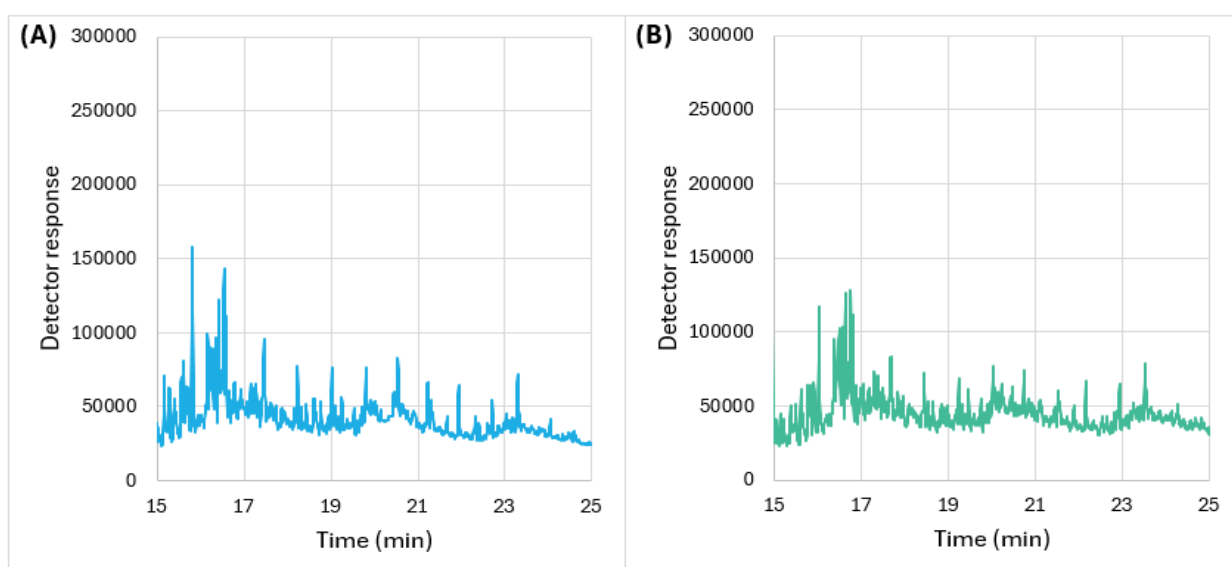


Figure 4-17: C₁₃ to C₂₀ segment of GC-MS chromatograms for the liquids derived from the TDOCM of virgin PP with initial pressures of (A) 15 bar and (B) 5 bar

Analysis of the gas yield, summarised in Figure 4-18, showed the higher-pressure runs also induced the same shift toward heavier compounds in the gas phase and a decrease in the amount of hydrogen and resulting olefins produced. As expected, increased reaction pressures suppressed gas-phase product formation, and this is due to two contributing factors. Firstly, higher reaction pressures increase the solubility of light gases, which in turn extends the residence time of these reactive intermediates, making them more likely to participate in the TDOCM sequence rather than volatilise to the gas phase before having a chance to react. Secondly, the increased reaction pressure also improves hydrogen solubility and availability on the catalyst surface, which promotes hydrogenation and (especially for PP) stabilises reactive fragments before they crack and escape into the gas phase.

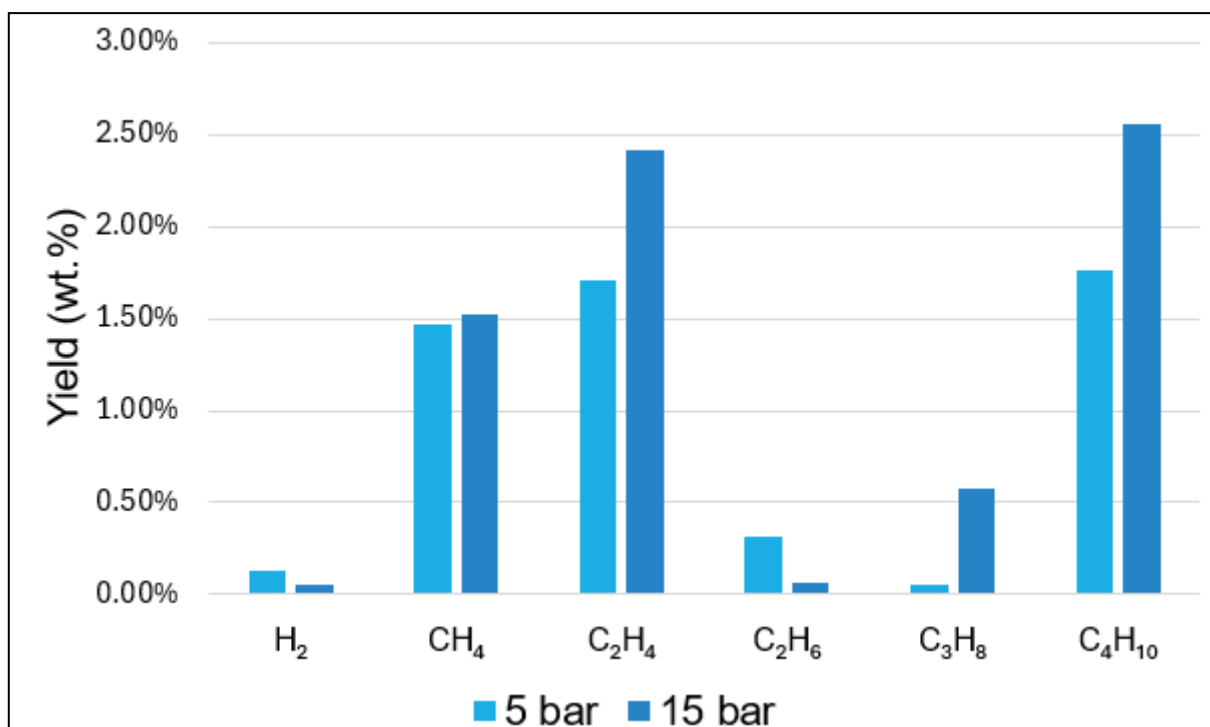


Figure 4-18: Comparison of the composition of the gas fraction derived from TDOCM of virgin PP and n-decane at 300°C for 3 hours, with a 1:5 catalyst to polymer ratio, 1:5 polymer to n-decane ratio for 5 bar vs. 15 bar initial pressure

Thus, for virgin PP at the given polymer to light alkane ratio, it is observed that increased reaction pressure does somewhat sway the product distribution to favour relatively heavier compounds; however, the more predominant factor influencing product distribution is still the light alkane to polymer ratio. It is also possible that increased reaction pressure could hinder the polymer's breakdown, as it would inhibit the dehydrogenation step by shifting the equilibrium toward the saturated reactants. To determine whether in fact this could be the case additional TDOCM experiments were performed on virgin LDPE at 300°C for 3 hours, with a 1:5 catalyst to polymer ratio, 1:10 polymer to n-decane ratio, with initial pressures of 5, 7.5 and 15 bar which afforded maximum reaction pressures of 35, 39 and 52 bar respectively (Run 2, 9, and 10).

The product distributions of the three experiments are depicted in Figure 4-19. It was observed that a slight increase in the initial pressure from 5 bar to 7.5 bar did not result in a noticeable change in the distribution of products derived from the TDOCM experiments. Both instances yielded roughly 20 ± 1.1 wt.% waxes and 70 ± 4.0 wt.% liquids, with the remainder reporting to the gas phase. Similarly, the composition of the liquid products was mostly unaffected when increasing the initial pressure from 5 to 7.5 bar, containing only alkanes, the majority of which ranged from C₁₃ to C₂₇; likewise, the composition of the gas phase also appeared to be unaffected by the small increase in pressure. Thus, the TDOCM system seems to be mostly unaffected by relatively small variations in reaction pressure. However, upon increasing the initial pressure to

15 bar, a considerable shift in the product distribution was observed. The mass decrease of the starting polymer remained at roughly 40% across the three experiments, but the amount of n-decane converted increased from 25 ± 0.8 wt.% for the 5 and 7.5 bar runs to 35 ± 0.8 wt.% for the 15-bar initial pressure run. Resultantly, the higher-pressure run yielded a much larger liquid fraction and significantly smaller gas yield compared to the 5 and 7.5 bar initial pressure runs.

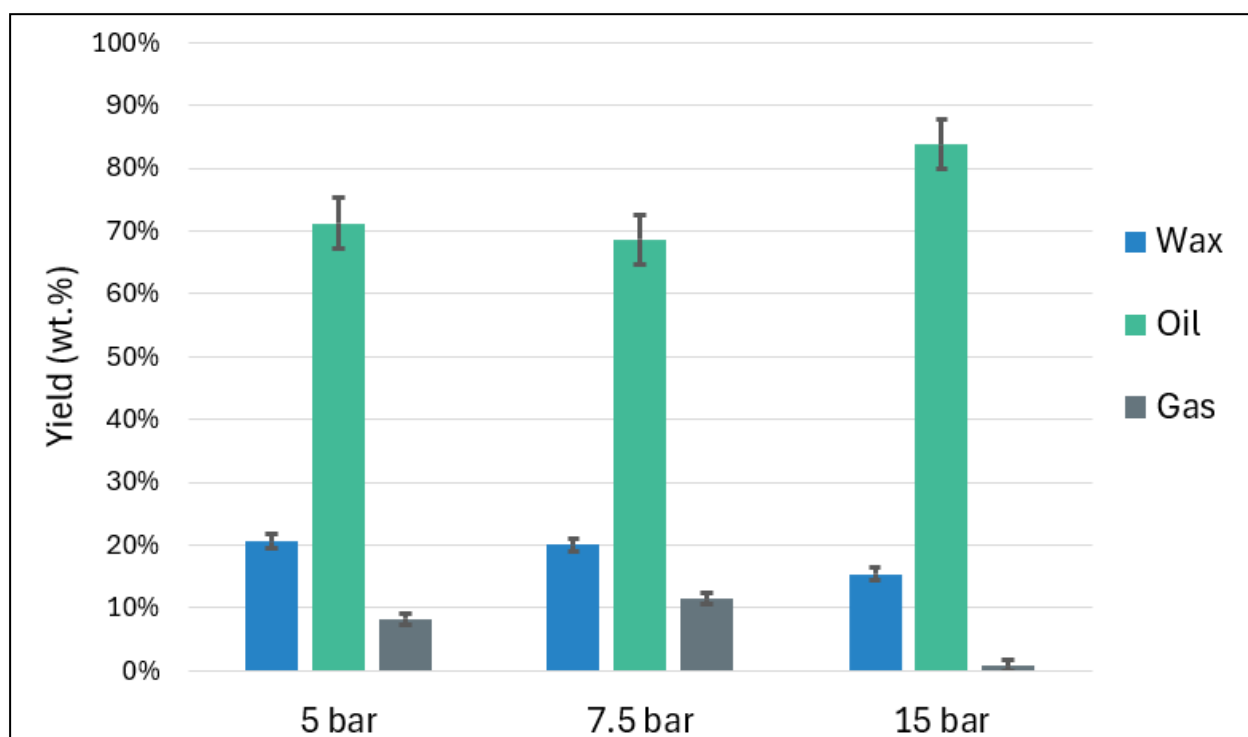


Figure 4-19: Product distribution of TDOCM experiments performed on virgin LDPE at 300°C for 3 hours, with a 1:5 catalyst to polymer ratio, 1:10 polymer to n-decane ratio and initial pressures of 5, 7.5 and 15 bar

GC-MS analysis of the liquid products also indicated a clear distinction between the composition of oils derived at 5 and 15 bar initial pressure. The oil derived at higher pressure still contained only alkanes; however, there was clear favour shown towards the formation of alkanes shorter than C_{19} when compared to lower-pressure runs, which is a result of the higher n-decane incorporation reducing overall product size. The improved n-decane conversion at higher pressures is likely due to improved solubility of H_2 at elevated pressures, as seen in the TDOCM experiments performed on virgin PP whilst also varying initial pressure. The dehydrogenation equilibrium inhibits the reaction to a lesser extent if H_2 remains dissolved rather than escaping to the reactor headspace. Additionally, at higher pressures, decane remains denser and more intimately associated with the catalyst phase, thereby improving its mass transfer to active sites and enhancing reaction kinetics.

It is thus concluded that, contrary to initial speculation, increasing the reaction pressure does not inhibit the TDOCM system by decreasing the dehydrogenation rate. Rather, increasing the

reaction pressure to the upper limit investigated in this study appears to improve decane incorporation by enhancing hydrogen solubility and the contact of the light alkane with catalyst active sites.

4.5.3 Effect of reaction time

The effect of reaction time on the quality and quantity of products derived from the TDOCM of PE with various light alkanes has been reported for several catalyst systems. It has been concluded that reaction time is an effective means to control the extent of polymer degradation and the average size of the derived alkanes, and as TDOCM is a continuous process, the reaction tends to proceed until the catalysts are severely deactivated. It is expected that the same trends would hold for the degradation of PP via TDOCM. To investigate the effect of reaction time on the product distribution and quality derived from PP, TDOCM experiments were performed on virgin PP at 300 °C for 3 hours, with a 1:5 catalyst-to-polymer ratio and a 1:10 polymer-to-n-decane ratio for 1 and 3 hours (Run 5 vs Run 12).

The product distributions of the two runs are summarised in Figure 4-20. The first observable feature is that the entire polymer sample was degraded to yield only liquid (81 wt.%) and gas (19 wt.%) products after 3 hours, whereas after 1 hour, 17.5 wt.% wax residues were recovered and liquid and gas yields reduced by 12 and 5 wt.% respectively.

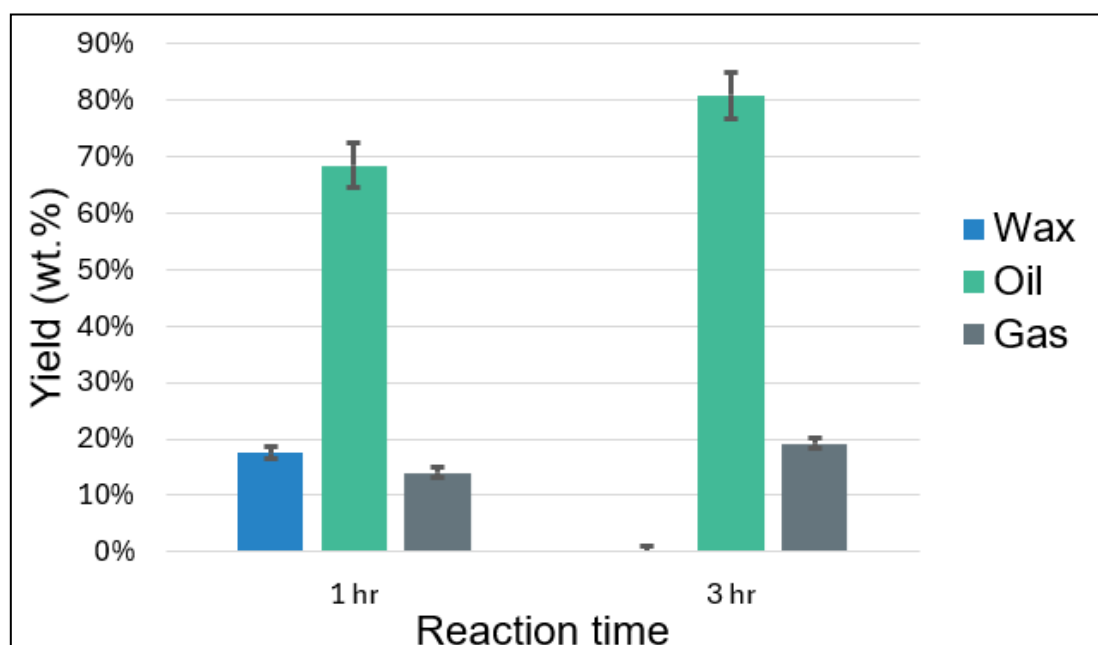


Figure 4-20: Product distribution of TDOCM experiments performed on virgin PP at 300°C for 3 hours, with a 1:5 catalyst to polymer ratio and 1:10 polymer to n-decane ratio for 1 and 3 hours, respectively

The starting virgin PP sample had a molecular weight of 250,000 g/mol and a polydispersity index (PDI) of 3.73. The recovered wax product after only 1 hour of reaction time had a molecular weight of 995 g/mol and a PDI of 2.6, with no trace of the initial polymer detected. This 99.6% decrease in molecular weight after just one hour indicates that the breakdown of the polymer chain occurs quite rapidly. Both experimental runs yielded liquid fractions comprised of alkanes ranging mostly from C₁₀ to C₂₀. The rapid breakdown of the starting polymer was also evident when comparing the composition of the liquid yields from the experiments. There was only slight favour shown toward large alkane production for the 1-hour runs compared to the 3-hour experiments, likely due to the shorter intermediates being just as rapidly degraded to even shorter products that would report to the gas yield. As a result, controlling the extent of degradation and the composition of products derived from the TDOCM of PP under these conditions could prove troublesome due to the rapid rate of degradation the sample displayed. Thus, varying alternative parameters such as catalyst loading ratios could be a more effective means of controlling product distributions.

4.5.4 Effect of catalyst loading ratio

Thus far, all reported TDOCM experiments have been performed at a 1:5 catalyst-to-polymer weight ratio. However, other researchers conducting similar work used more than double this loading ratio, thus, to compare the performance of the WO_x/SiO₂ and Pd/γ-Al₂O₃ catalyst system used in this work to existing studies and to understand its effect on product distribution and quality, TDOCM experiments were performed using virgin HDPE and LDPE with a 1:2 and 1:5 catalyst to polymer weight ratios at 300°C for 3 hours, with a 1:10 polymer to n-decane ratio and 5 bar initial pressure (Runs 1 & 2 vs. Runs 13 & 14).

The product yields of the 1:2 and 1:5 (catalyst-to-polymer loading ratio) experiments are summarised in Figure 4-21.

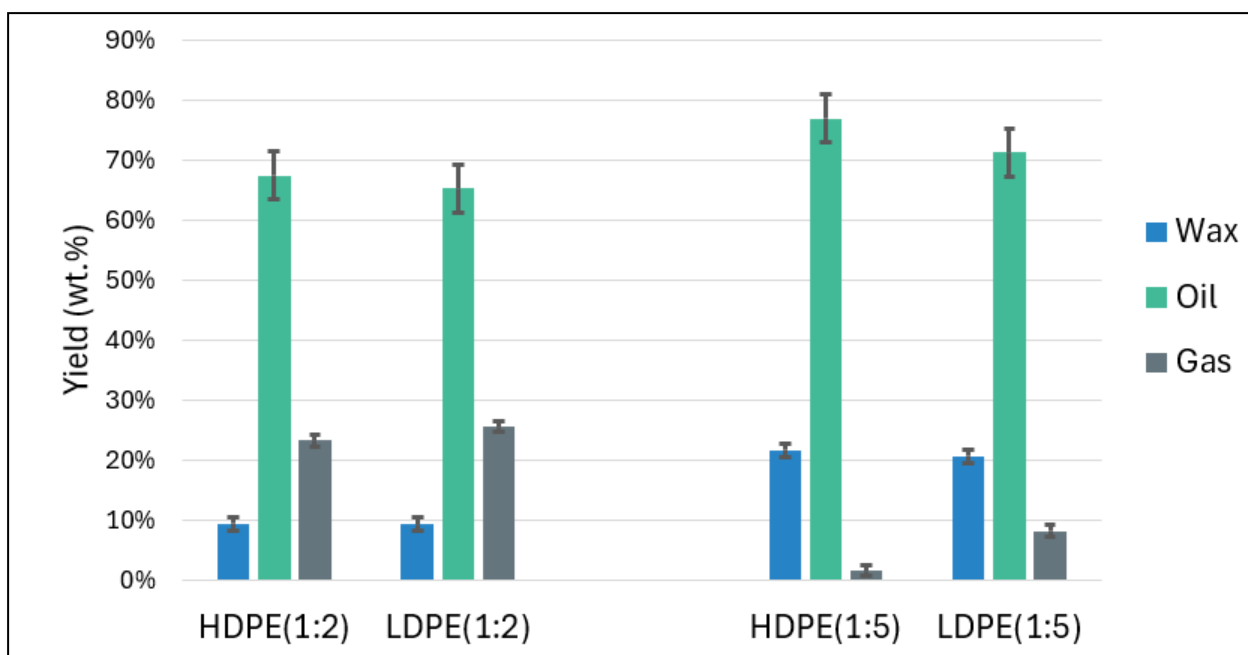


Figure 4-21: Comparison of the product distribution of TDOCM experiments using 1:2 and 1:5 catalyst to polymer weight ratios performed at 300°C for 3 hours, with a 1:10 polymer to n-decane ratio and 5 bar initial pressure

Expectedly, wax yields were halved from around 20 wt.% to just under 10 wt.% for both HDPE and LDPE when increasing the catalyst to polymer weight ratio from 1:5 to 1:2. This indicates a more extensive breakdown of the initial polymer chains in the same amount of time when the amount of catalyst is increased. This is attributed to the higher availability of active sites that promote the dehydrogenation of the polymer backbone and the subsequent metathesis reactions. Interestingly, liquid yields were mostly unaffected by the change in catalyst loading ratio, whereas the gas yields increased from 2.5 wt.% to 23 wt.% for virgin HDPE and from 8 wt.% to 25.5 wt.% for virgin LDPE with the increase in catalyst loading ratio. Additionally, the composition of the liquid fractions derived was nearly identical and appeared to be independent of the catalyst loading ratio. Likewise, the n-decane conversion for both PE types remained unchanged at roughly 20 ± 0.8 wt.%. Thus, if more n-decane was not incorporated into the polymer chains to achieve the more extensive degradation seen at higher catalyst loading, the only conclusion is that polymer chains with terminally unsaturated sites had to react with one another. Instead of decene then being incorporated into the polymer chains and leading to gradually smaller fragments, metathesis between two ends of the polymer chains would systematically cleave small fragments from the main polymer chains, eventually leading to large, short alkane yields, but still a quite significant breakdown of the starting polymer. This argument aligns with the derived product distributions and explains the significant increase in the gas fractions observed.

Similarly, when experiments were performed on virgin PP under the same reaction conditions while only altering the catalyst-to-polymer weight ratio from 1:5 to 1:2 (Run 5 vs Run 15), the same trend in product distribution was again observed. The liquid yield only decreased by 5 wt.% from 81 wt.% to 76 wt.% with no solid residue recovered in either of the experimental runs. As with the PE runs, n-decane conversion was not influenced by catalyst amount and remained at 26 ± 0.8 wt.%. It is concluded that n-decane conversion is likely equilibrium-limited rather than kinetically limited under the examined conditions. However, polymer degradation continues because polymer dehydrogenation, unlike that of small alkanes, is not governed by a simple reversible equilibrium. The generation of unsaturation at multiple sites along the polymer backbone, followed by metathesis and hydrogenation steps, can proceed continuously if sufficient catalyst is present.

Table 4-5 summarises how this study compares with others that also investigate TDOCM utilising a heterogeneous catalyst pairing to degrade PE.

Table 4-5: Comparison of TDOCM results in recent literature

Reference	This work	(Moore et al., 2025)	(Kim et al., 2022)	(Ellis et al., 2021)	(Jia et al., 2016)
Olefin metathesis catalyst (metal loading, wt.%), quantity (g)	WO _x /SiO ₂ (1.8), 01	Re ₂ O ₇ /γ-Al ₂ O ₃ (10), 0.5	WO _x /SiO ₂ (2), 0.8	Re ₂ O ₇ /γ-Al ₂ O ₃ (8), 0.5	Re ₂ O ₇ /γ-Al ₂ O ₃ (5), 0.5
(De)hydrogenation catalyst (metal loading, wt.%), quantity (g)	Pd/γ-Al ₂ O ₃ (0.5), 1	Pd/γ-Al ₂ O ₃ (1.0), 0.5	Pt/γ-Al ₂ O ₃ (1.0), 0.5	SnPt/γ-Al ₂ O ₃ (1.7, 0.8), 0.5	Ir complex/γ-Al ₂ O ₃ , 4.2 μmol (Ir basis)
PE, quantity (g)	HDPE, 5	HDPE, 0.28	LDPE, 1.6	HDPE, 0.13	LDPE, 0.12
Short alkane, quantity (g)	n-decane, 50	n-pentane, 18.8	n-decane, 9.6	n-pentane, 18.8	n-octane, 2.8
Short alkane/PE ratio (g/g)	10	66.7	6	144.5	23.4
Reaction temperature (°C)	300	190	300	200	175
Reaction time (h)	3	15	3	15	96
M_n of virgin PE (kDa)	165	11.4	9.1	17.9	5.1
M_n of wax (kDa)	16	0.11	0.68	2.6	1.1

As seen from Table 4-5, this study managed to reduce the number average molecular weight of the starting PE sample by 90% after a reaction time of only 3 hours, using less than half the amount of catalyst that the next comparable study does (Kim et al., 2022). This firstly illustrates the increased activity of Pd/ γ -Al₂O₃ over Pt/ γ -Al₂O₃ when comparing this study to the work of Kim et al. (2022), who also made use of WO_x/SiO₂ as the metathesis catalyst but opted for Pt/ γ -Al₂O₃ as their dehydrogenation catalyst. Secondly, this illustrates the advantage of being able to operate at 300 °C due to the increased thermal stability of WO_x/SiO₂ over Re₂O₇/ γ -Al₂O₃ as Moore et al. (2025) and Ellis et al. (2021) could only achieve similar extents of degradation after 15 hours, as they were limited to 200 °C reaction temperatures by their metathesis catalyst (Re₂O₇/ γ -Al₂O₃). By demonstrating that using relatively less of the more reactive Pd/ γ -Al₂O₃ dehydrogenation catalyst and operating at higher temperatures with the WO_x/SiO₂ metathesis catalyst, which is much more affordable than Re₂O₇/ γ -Al₂O₃, this study has made significant advances in improving the economics of the catalyst system used in TDOCM of PE with light alkanes.

This study also utilised the highest molecular weight PE yet reported, with a molecular weight more in line with those of consumer-grade examples. This builds on the proof-of-concept type studies and illustrates that TDOCM could potentially be applied to actual PE waste, illustrating its viability as a recycling scheme.

Finally, this study also operated at one of the lowest light alkane-to-polymer ratios seen in reported works. Using less light alkane as a co-reactant will also improve the economics surrounding TDOCM as a recycling scheme. Additionally, the light alkane-to-polymer ratio used in this work highlighted the role of the light alkane not only as a co-reactant, but as a heat sink, and conduction and reaction medium, an important role not reported by other studies.

4.6 Alternative light alkanes to improve economic feasibility

Petroleum ethers are a petroleum fraction that boils in the 40 to 60 °C range. They consist mostly of aliphatic hydrocarbons (pentanes and hexanes) and are more widely available and significantly less expensive than n-decane. Additionally, because of the volatility of petroleum ether, it can easily be separated from the TDOCM products by distillation. Thus, petroleum ether and similar cheap and practical light alkane alternatives can significantly improve the economic feasibility of the TDOCM process as a polyolefin recycling scheme.

To study the efficacy of PE breakdown using petroleum ether as a metathesis reagent, a TDOCM experiment was performed using virgin HDPE (5g) and petroleum ether (50g) at 300 °C for 3 hours, with the proven WO_x/SiO₂ and Pd/ γ -Al₂O₃ catalyst system at a 1:5 catalyst to polymer

weight ratio and 15 bar initial pressure. After an additional distillation step, roughly 8g of liquid product with a boiling point above 60 °C was recovered, the GC-MS chromatogram of this liquid

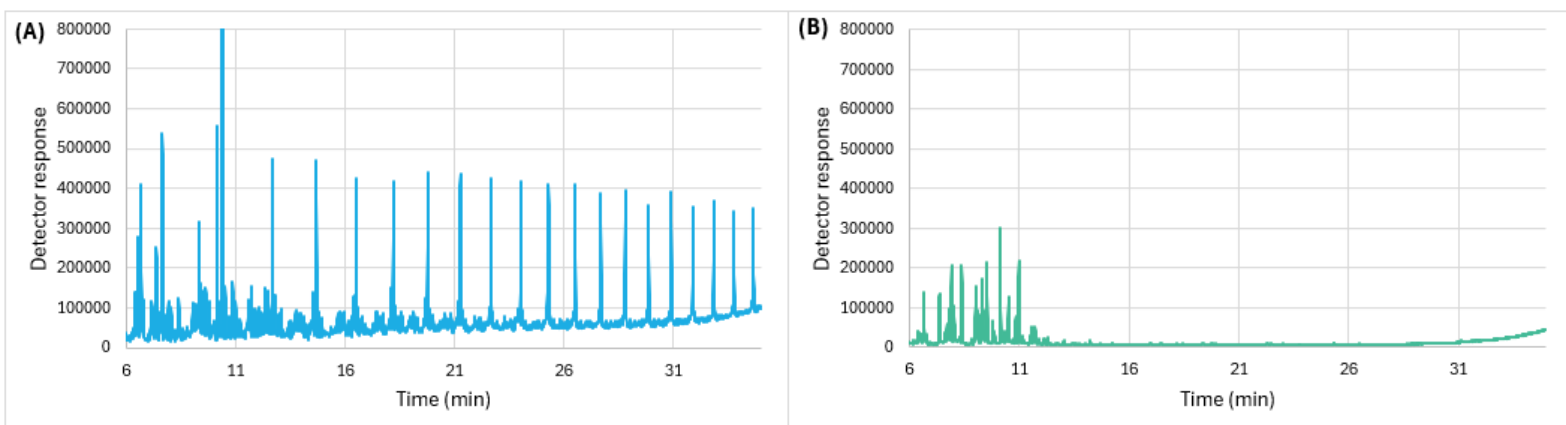


Figure 4-22: GC-MS chromatograms of the C₉ to C₂₀ range of (A) oil derived from TDOCM experiment performed on virgin HDPE and petroleum ether, and (B) unreacted petroleum ether as reference

fraction, along with that of a petroleum ether blank, is depicted in Figure 4-22.

The GC-MS analysis revealed that the recovered oil fraction consisted nearly entirely of alkanes, with the majority falling within the diesel fraction (C₉–C₂₂). It was also observed that using petroleum ether resulted in slightly more iso-alkanes being formed when compared to experimental runs using n-decane. This is not surprising, as analyses revealed that most of the petroleum ether consisted of pentanes or hexanes with up to four methyl groups attached in some instances. Figure 4-22(B) also revealed that the petroleum ether sample contained small amounts of xylene and benzene. Similar quantities of these two compounds were also detected in the oil fraction recovered after the TDOCM experimental run, which suggests that the aromatics act as spectators and are not incorporated into the polymer structure by some means.

The reactor was purged and pressurised to 15 bar using N₂, before heating commenced. This resulted in a maximum reaction pressure of 75 bar (close to the upper limit of the reactor). As in the n-decane experiments, elevated pressure suppressed gas formation, resulting in a negligible gas yield in the TDOCM experiment using petroleum ether.

Lastly, approximately 5g of wax product was recovered. This was somewhat unexpected, as the liquid product clearly indicates the occurrence of cross-incorporation between the starting polymer and the petroleum ether, yet the solid product mass matches that of the starting polymer. The wax product could not be subjected to GPC analysis due to its high cost; thus, its molecular weight is unknown. However, it is likely that the wax product has a very narrow PDI, meaning petroleum ether is evenly incorporated into all polymer chains; however, not to such an extent that the polymer's molecular weight is decreased enough for the residual product to be liquid at room temperature. Nevertheless, petroleum ether shows great promise in improving the economics of

TDOCM as a recycling scheme, as it adds value to both the starting polymer and the petroleum ether.

CHAPTER 5 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The conclusions derived from the results of this study and how they relate to the initial objectives can be summarised as follows:

5.1.1 Objective 1

Objective: Characterise the polymer feedstocks and the catalysts using advanced analytical techniques.

Virgin, recycled, and commercial-grade HDPE, LDPE, and PP samples were utilised in this study. Virgin HDPE, LDPE and PP samples had number average molecular weights of 165 000, 30 000, and 67 000 g/mol, respectively. These virgin samples were free of additives or pigments but had molecular weights in line with commercial grade equivalents, allowing for the study of how the catalyst pairing would handle these larger molecular weights without additives or pigments inhibiting the results. Recycled and commercial-grade samples were included to study the effect that additives such as calcium carbonate and Irganox would have on catalyst performance.

Both WO_x/SiO_2 and $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ could be classified as mesoporous materials, with $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ having a slightly less intricate pore structure than WO_x/SiO_2 . Additionally, it was concluded that the catalyst pretreatment step did not have any significant impact on the chemical composition, crystalline structure or surface morphology of either of the two catalysts.

5.1.2 Objective 2

Objective: Test the efficiency of the catalyst system in degrading polymer samples.

Control experiments revealed that the catalyst pairing of WO_x/SiO_2 and $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ did indeed have a catalytic effect on the system and incorporated n-decane into the HDPE structure to result in a 90% decrease in the molecular weight of the starting virgin HDPE material and yield nearly 70 wt.% liquid products. Additionally, the system showed excellent selectivity towards alkane formation, as nearly all products identified in the wax, oil, and gas product fractions consisted only of alkanes. Furthermore, using the catalyst pairing of WO_x/SiO_2 and $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ and operating at 300 °C, this study achieved the same extent of PE degradation in a quarter of the time and using half the amount of catalyst that other researchers required.

5.1.3 Objective 3

Objective: Investigate the applicability of the catalyst system on other polymer grades and types.

It was also observed that WO_x/SiO_2 and $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ could degrade virgin LDPE as well as recycled and consumer grade PE samples via TDOCM to the same extent as virgin HDPE, to again yield ≥ 70 wt.% oils, with only alkanes identified in the product fractions. Thus, the system does not appear to be inhibited by PE structure nor the presence of additives, improving the viability of TDOCM as a potential recycling scheme, as no additional sorting between different PE grades would be required.

Additionally, this is the first work to illustrate the degradation of PP via TDOCM. Applying TDOCM to virgin PP completely degraded the starting polymer to yield only liquid (81 wt.%) and gas (19 wt.%) products. Similar to PE, when applying TDOCM to PP, the process yields almost entirely alkanes, with PP showing a preference for iso-alkane formation.

5.1.4 Objective 4

Objective: Identify and evaluate the predominant factors influencing the yield and composition of products.

Further experiments revealed that reaction pressure, reaction time, light alkane-to-polymer ratios, catalyst-to-polymer ratios, and the light alkane type would all influence the product quality and quantity.

The amount of light alkane present in the system had the most significant effect on product quality and yields, as decreasing the amount of light alkane would promote redundant polymer-polymer cross reactions for PE, reducing the extent of PE degradation and nearly doubling wax yields, or promote a secondary mechanism of β -scission for PP which did not reduced the extent of PP degradation but did lead to the formation of unsaturated products, reducing the selectivity of the TDOCM process.

Increased reaction pressure increased the extent of polymer degradation and promoted the formation of larger alkanes, as light intermediates would rather remain in the reaction pool at higher pressures to further partake in the TDOCM loop. Resultantly, increasing the initial reaction pressure from 5 bar to 15 bar increased oil yields by 15 wt.% whilst decreasing wax yields by nearly 10 wt.%. Again, only alkanes were detected in the product fractions.

Finally, the TDOCM mechanism could also be applied to PE and inexpensive petroleum fractions. Using petroleum ether, which consisted mostly of isopentane and isohexane, and virgin HDPE, a

liquid fraction containing only alkanes, most of which in the C₉ to C₂₀ range could be derived. Thus, TDOCM also offers a viable means of upgrading PE waste and inexpensive petroleum fractions.

5.2 Recommendations

- Variations in catalyst pretreatment and activation procedure were omitted from this study and could likely influence catalyst activity
- Catalyst activity with time remains to be explored, along with possible regeneration procedures
- A more detailed study of reaction kinetics would be beneficial in better understanding catalyst behaviour
- Focus should be given on decreasing the amount of catalyst required and exploring whether more inexpensive metals are capable of such chemistry to improve associated economics
- Investigate alternative light alkanes to improve reaction economics
- Additional post-reaction processing of liquids to obtain desirable fractions or derive transportation fuels can be investigated
- Future work may perform techno-economic studies to justify the feasibility of TDOCM viable PE and PP waste recycling scheme.

Acknowledgements

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ANNEXURE A: REPEATABILITY

Table A-1 and A-2 show the product fractions of triplicate runs performed at the described process conditions. The confidence interval was calculated according to Section 3.11. The average error on a 95% confidence interval was determined to be 0.7%, 3.9% and 0.3% for the wax, oil and gas fractions respectively.

Table A-1: Product fractions of repeat runs performed on HDPE at 300°C for 3hr with a 10:1 solvent to plastic ratio and a 1:5 catalyst to plastic ratio

	Run 1	Run 2	Run 3	Average	Standard deviation	Confidence Interval
Wax	8.7%	8.4%	8.8%	8.6%	0.2%	8.6±0.6%
Oil	90.8%	92.9%	94.7%	92.8%	1.6%	92.8±4.8%
Gas	0.5%	0.0%	0.0%	0.2%	0.2%	0.2±0.7%

Table A-2: Product fractions of repeat runs performed on LDPE at 300°C for 3hr with a 10:1 solvent to plastic ratio and a 1:5 catalyst to plastic ratio

	Run 1	Run 2	Run 3	Average	Standard deviation	Confidence Interval
Wax	6.4%	5.7%	5.7%	5.9%	0.3%	5.9±0.9%
Oil	93.9%	96.0%	96.0%	95.3%	1.0%	95.3±3.1%
Gas	0.0%	0.0%	0.0%	0.0%	0.0%	0±0%

Triplicate decane quantification analyses were also performed on three different oil samples derived from LDPE, HDPE and PP at 300 °C for 3hr with a 10:1 solvent to plastic ratio and a 1:2 catalyst to plastic ratio. The percentage of decane calculated with each analysis for each sample are shown in Table A-3. The average error, for the decane quantification method, on a 95% confidence interval was determined to be 0.8%.

Table A-3: Amount of decane present (wt.%) in the oils derived from DCAM experiments performed on LDPE, HDPE and PP at 300°C for 3hr with a 10:1 solvent to plastic ratio and a 1:2 catalyst to plastic ratio

	Analysis 1	Analysis 2	Analysis 3	Average	Standard deviation	Confidence Interval
LDPE	81.0%	80.7%	80.6%	80.8%	0.2%	80.8±0.6%
HDPE	79.1%	79.0%	79.5%	79.2%	0.3%	79.2±0.7%
PP	74.7%	73.9%	74.1%	74.3%	0.4%	74.3±1.1%

From Equation 10 the overall error associated with the wax, oil and gas fractions are then 1.1%, 4.0% and 0.9% respectively.

ANNEXURE B: CALIBRATION CURVES

GPC calibration

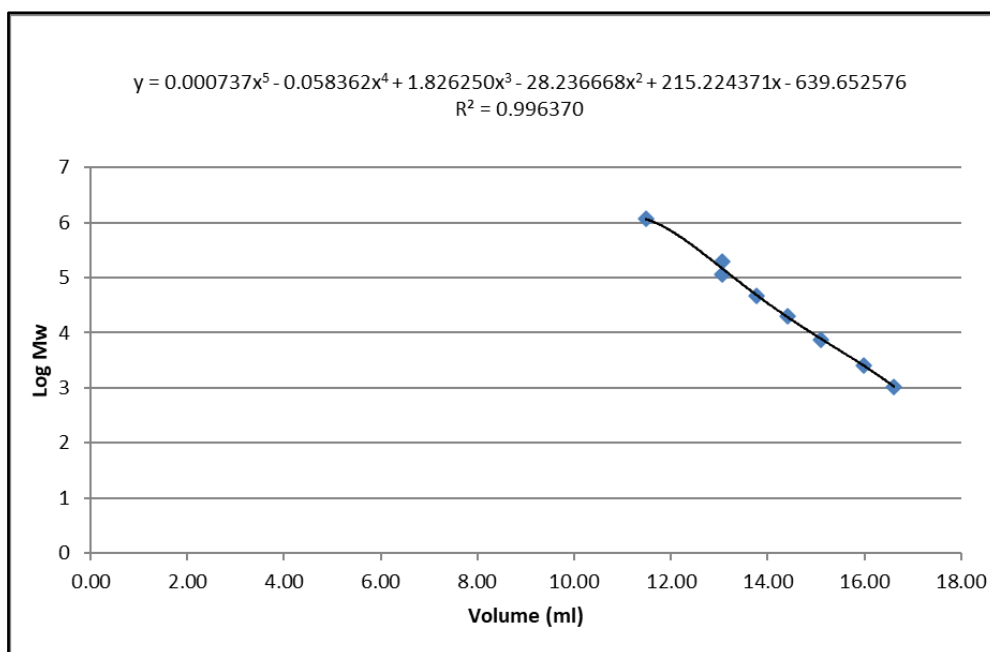


Figure B-1: GPC calibration curve relating elution volume to Log Mw

GC-FID calibration

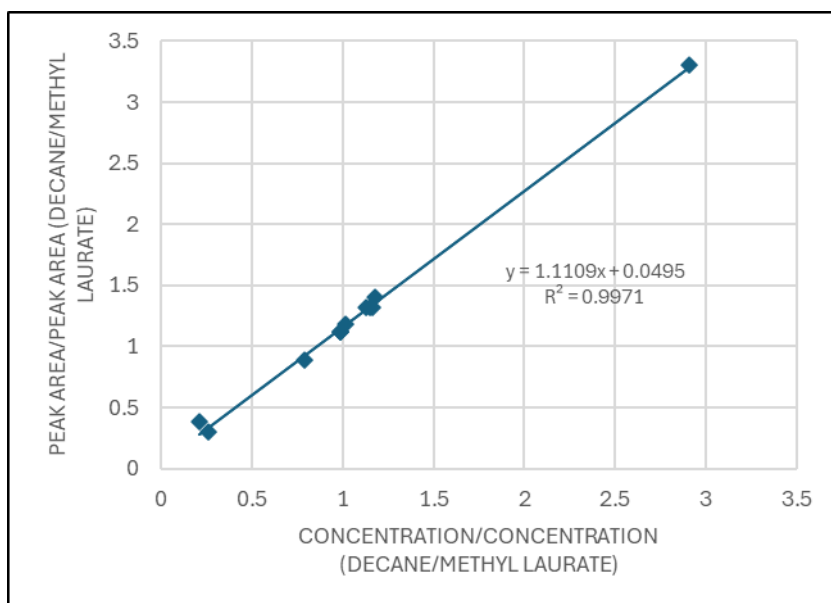


Figure B-2: GC-FID calibration curve relating the decane IS concentration ratio to the decane IS peak are ratio

The decane concentration could then be calculated using Equation 12 as follows:

$$C_D = C_I \times \frac{\frac{A_D}{A_I} - 0.0495}{1.1109} \quad \text{Eq. 12}$$

Where:

C_I refers to the concentration of the internal standard and A_D and A_I refer to the peak areas of the decane and internal standard peaks respectively.

ANNEXURE C: SUPPORTING RESULTS

Initial catalyst system testing and control experiments

Figure C-1 and C-2 show the FTIR spectra of the liquid and wax fractions respectively, recovered after TDOCM experiments using virgin HDPE and n-decane. Both spectra only indicate the presence of bonds coinciding with alkanes.

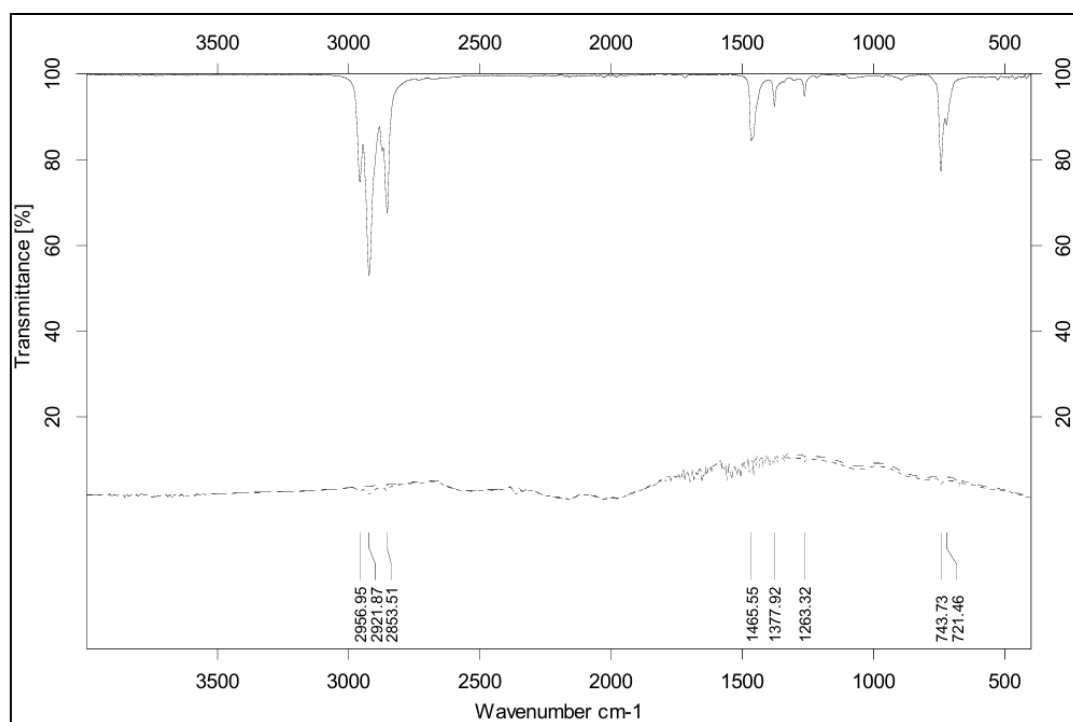


Figure C-1: FTIR spectra of the liquid fraction obtained from the TDOCM experiment of virgin HDPE and n-decane at a 1:10 weight ratio with a 5:1 plastic to catalyst weight ratio. The experiment was performed at 300°C for 3 hours

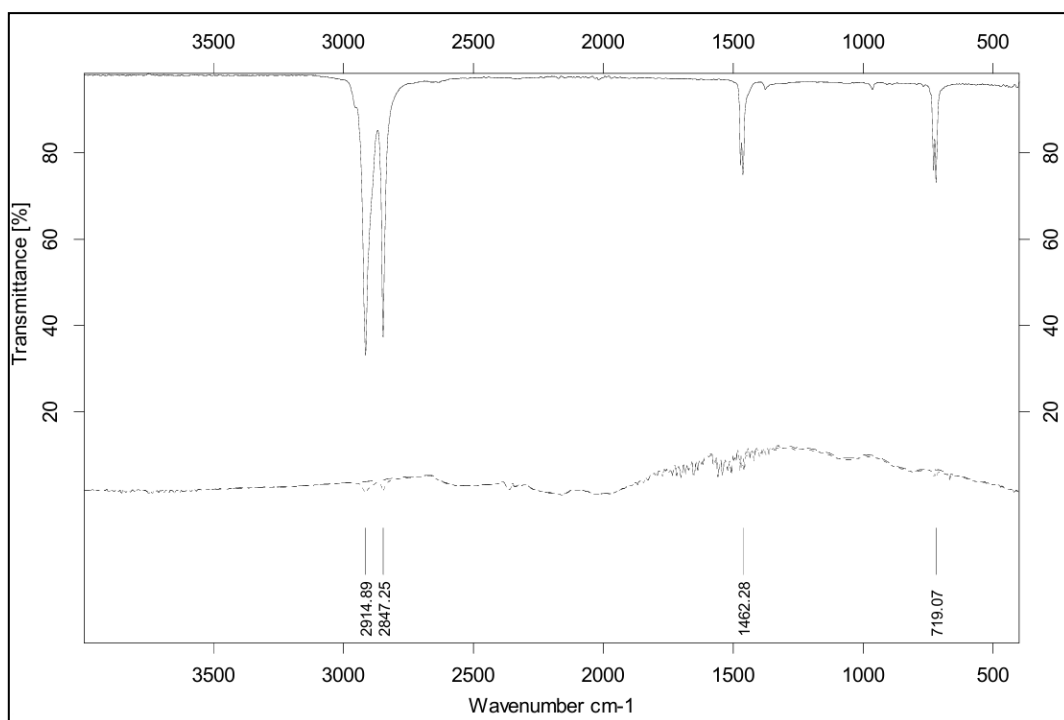


Figure C-2: FTIR spectra of the solid fraction obtained from the TDOCM experiment of virgin HDPE and n-decane at a 1:10 weight ratio with a 5:1 plastic to catalyst weight ratio. The experiment was performed at 300°C for 3 hours

Figure C-3 compares the composition of the gas fractions derived from control experiments when either the dehydrogenation or metathesis catalyst was omitted.

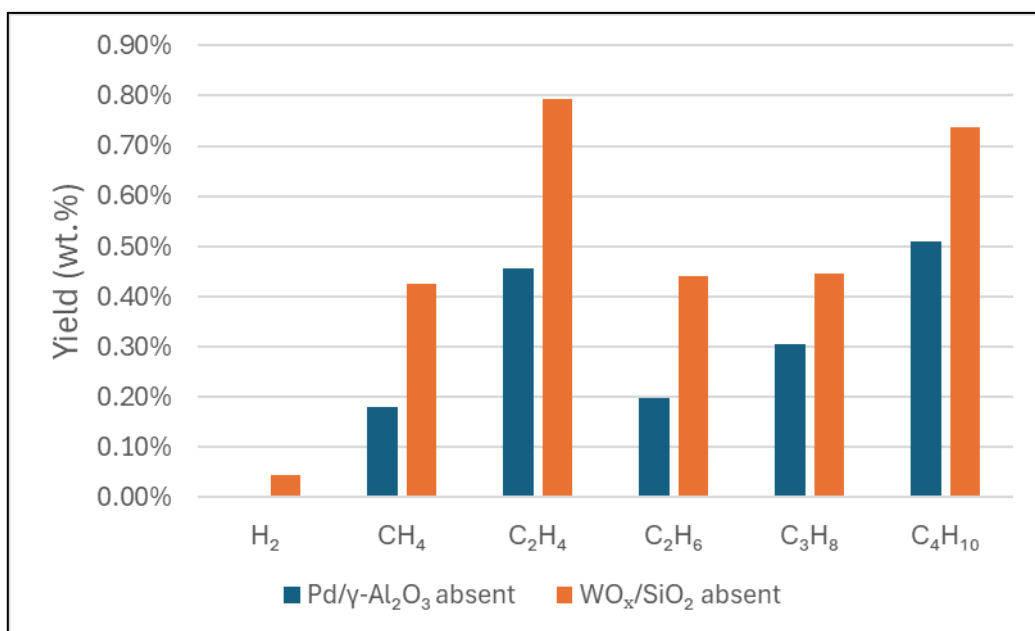


Figure C-3: Composition of the gas fractions obtained from experimental results when either Pd/γ-Al₂O₃ or WO_x/SiO₂ was omitted

Figure C-4 illustrates the composition of the gas fraction derived from a TDOCM experiment performed on virgin HDPE and n-decane at 300°C for 3 hours, with a 1:5 catalyst to polymer ratio and polymer to n-decane weight ratio of 1:10 compared to the gas fraction of derived from an experiment at the exact same conditions but with no polymer present in the reactor.

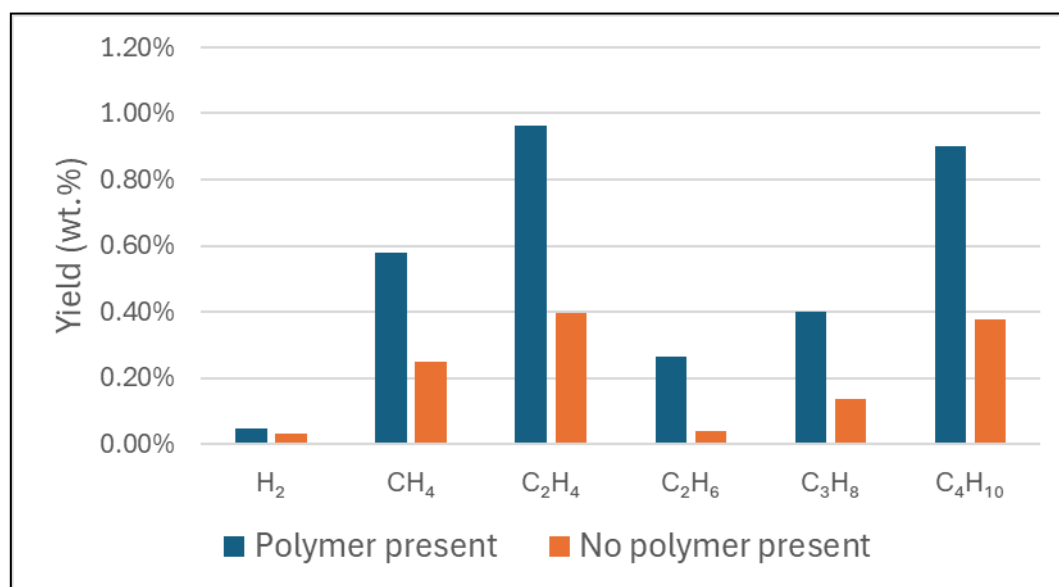


Figure C-4: Difference in the composition of the gas fraction when no polymer is present in the reactor

The greater abundance of larger hydrocarbons for the run with polymer present is a further indication of the cross-incorporation of polymer and n-decane.