TALLINN UNIVERSITY OF TECHNOLOGY

SCHOOL OF ENGINEERING

Department of Mechatronics

STUDIES ON THE CO-PYROLYSIS OF OIL SHALE AND BIOMASS

PÕLEVKIVI JA BIOMASSI KOOSPÜROLÜÜSI UURINGUD

MASTER THESIS

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Tallinn 2021

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Studies On The Co-Pyrolysis Of Oil Shale And Biomass

Supervised by: Oliver Järvik

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17/05/2021

TTÜ Department of Power Electronics and Mechatronics

THESIS TASK

Student: Alabi Oluwashola

Study programme: Master’s Degree in Mechatronics

Supervisor(s): Oliver Järvik, senior researcher

Co-supervisor: Sepehr Mozaffari

Thesis topic:

(in English) STUDIES ON THE CO-PYROLYSIS OF OIL SHALE AND BIOMASS

(in Estonian) PÕLEVKIVI JA BIOMASSI KOOSPÜROLÜÜSI UURINGUD

Thesis main objectives:

1. Investigate the co-pyrolysis behavior of oil shale and biomass.
2. Produce a pyrolysis oil/tar with a high heating rate value.
3. Characterization of oil/tar and solid residue.

Thesis tasks and time schedule:

No	**Task description**	**Deadline**
1.	Literature overview	15/12/2020
2.	Pyrolysis and co-pyrolysis experiments of feedstock	24/04/2021
3.	Analyze the results obtained from experiments	08/05/2021

Language: English **Deadline for submission of thesis:** 18th May 2021

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PREFACE

I would like to thank God for making all this possible, he made my dream come through and also gave me the privilege of completing this thesis.

I would like to show my deepest gratitude to my supervisor, Oliver Järvik the Head of Centre Department of Energy Technology Tallinn University of Technology for giving me the support and opportunity to do my research work, I say thank you. And to my co-supervisor Sepehr Mozaffari thank you for your experience and support in guiding me through the experimental process, I am grateful.

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The current study is on the co-pyrolisis of Oil shale and Biomass. It is aimed at studying the behavior and improving the overall properties and qualities of Biomass while producing sustainable oil/tar that would have applications in industries.

KOKKUVÕTE

Biomassist bio-õlide tootmise alased uuringud muutuvad järjest aktuaalsemaks, kuna bio-õlisid peetakse üheks fossiilsete kütuste asendajaks. Bio-õlida kasutamisel on aga probleemiks see, et nende omaddused on fossiilsete kütuste baasil toodetud õlidest tunduvalt erinevad, mis muudab esimeste rakendamise keeruliseks. Üheks võimaluseks bio-õlide baasil toodetud õlide omaduste parandamiseks on peetud õli tootmist biomassi ja fossiilsete kütuste koospürolüüsil.

Käesoleva töö eesmärgiks oli uurida biomassi ja põlevkivi koospürolüüsi. Protsessi uuriti termogravimeetrilises analüsaatoris (TGA) ja Fischeri analüüsiga, kasutades madalat kuumutuskiirust (10°C/min). Koospürolüüsil kasutati lähtematerjalina põlevkivi ja biomassi (puit; must lepp) segusid massi järgi vahekordades 100:0, 0:100, 30:70, 50:50 ja 70:30. TGA-d kasutati massi muutuste uurimiseks ning Fischeri analüüsiga toodeti heterogeenne õli ja pürolüüsivee segu (pürolüüsivedelik). Tulemused näitasid, et biomassi osakaalu suurenemisel lähtematerjalis kasvas kuumutamisel massikadu. Saadud pürolüüsivedeliku iseloomustamiseks mõõdeti tema erinevaid füüsikalis-keemilisi omadusi: tihedus, murdumisnäitaja, viskoossus ja kütteväärtus. Tulemused näitasid, et põlevkivi pürolüüsil saadud õli kütteväärtus oli kõige kõrgem. Pürolüüsivedelike koostise analüüsiks kasutati gaaskromatograaf-massdetektor-leefotoionisatsioondetektor süsteemi. Sellega analüüsiti õlides leiduvaid ühendeid ning spetsiifiliselt ka väävliühendeid. Võrreldes erinevaid õlisid, leidus väävliühendeid kõige rohkem põlevkiviõlis ning lähtematerjalides puidu osakaalu kasvades väävlisisaldus pürolüüsivedelikus vähenes.

Töö tulemused näitavad, et pürolüüsiõlide kvaliteedi tõstmiseks läbi puidu ja põlevkiv koospürolüüsi, on vajalik teostada täiendavaid uuringuid. Eeldatavalt võiks materjalide kuumutuskiiruse märgataval tõstmisel saada homogeense koostisega õli, mille omadused on võrreldes bio-õliga sobivamad kasutamiseks olemasolevates süsteemides.

Märksõnad: kukersiitne põlevkivi, biomass, põlevkiviõli, bio-õli, koospürolüüs

ABSTRACT

The number of studies on biomass pyrolysis for producing bio-oil is increasing as bio-oil is expected to replace fossil fuels. However, bio-oil properties are different from fossil oils, making their implementation in different applications difficult. One option that has been proposed to obtain the oil with improved properties is the co-pyrolysis of biomass and fossil fuel.

The goal of the thesis was to study the co-pyrolysis of oil shale and biomass. The process was investigated by thermogravimetric analysis (TGA) and Fischer assay at 520 °C using low heating rates (10°C/min). Oil shale and biomass (wood; black alder) were prepared as feedstock in ratios 100:0, 0:100, 30:70, 50:50, and 70:30 by weight. TGA was used to study the mass loss while the Fischer assay was used for the production of pyrolysis liquid (heterogeneous mixture of oil and water). Ratios with higher biomass content had a higher mass loss and oil yield when compared to ratios with high oil shale content. Experimental analysis was carried out on the pyrolysis liquid to study properties like density, refractive index, viscosity, and heating value. The heating value of shale oil produced was the highest and ratios with high oil shale content produced pyrolysis liquid with higher heating values when compared to ratios with high biomass content. Gas chromatography-mass spectrometry (GC-MS) was used to identify different volatile compounds in the pyrolysis liquid, while GC-flame photometric detector (GC-FPD) was used to detect sulfur compounds in the pyrolysis liquid. When compared to the rest of the oils produced, shale oil contained the most sulfur and this trend could be noticed across the different ratios as ratios with high oil shale content had more sulfur compounds.

The results of this thesis suggest that further studies for improving the quality of the pyrolysis liquid from the co-pyrolysis process are needed. It is expected that using pyrolysis with a higher heating rate would produce a more homogeneous pyrolysis liquid with improved properties.

Keywords: Kukersite oil shale, Biomass, Shale oil, Bio-oil, Co-pyrolysis

List of abbreviations and symbols

OS	Oil Shale
BM	Biomass
HHV	Higher Heating Value
LHV	Lower Heating Value
TGA	Thermogravimetric analysis
FA	Fischer Assay
GS-MS-FPD	Gas Chromatography-Mass-Flame Photometric Detector

1. INTRODUCTION

Due to the increase in CO_2 level in the world because of the combustion of fossil fuels, an increase in demand for energy has prompted more research and development of an alternative and more sustainable energy source [1].

Bioenergy, a renewable in the form of biomass and biofuels has had an increase in research and development studies for a couple of years because of its availability in large quantities in different regions of the world and the ability to harness its potential in the energy field [2]. Biomass has a lot of advantage and one of its important advantages is that it absorbs carbon dioxide during photosynthesis: as a result of this, biomass can be carbon neutral if fossils fuel are not used during the growth, collection, transportation, processing, plant construction, development, or decommissioning stages [2].

Oil shale, a sedimentary rock with an organic matter known as kerogen when heated produces liquid and gaseous hydrocarbons similar to that produced by crude oil and has a potential for diverse industrial applications due to its large reserves, and because of this, oil shale is considered as one of the major substitute energy resources for petroleum [3], [4]. In Estonia, there are existing technologies for oil shale processing (pyrolysis), however, due to climate concerns a focus-driven research on substituting (at least partially) oil shale with biomass or wastes (plastics) in these technologies.
During the retorting of kerogen in oil shale, oil shale starts to decompose at 350 ^{o}C, and as temperature continues to increase the decomposition process is further accelerated and further broken to shale oil, gas, semicoke, and water [5]. While for biomass, pyrolysis at about 250-400 °C produces bio-oil, gases, and coke [6]. Oil shale is a low-grade fossil fuel currently used for the generation of electricity and has been used in Estonia mostly for electricity and shale oil production [8]. Biomass-derived fuels make up to 37% of the primary energy content of the fuels used in the region of Southern-Estonia [9].

Co-pyrolysis is a thermal decomposition that involves two or more materials. Co-pyrolysis helps improve the characteristics of pyrolysis oil as shown in many scientific research work [7]. With this in mind, the task of the thesis is to study the co-pyrolysis of oil shale and biomass with the focus on the characterization of oil/tar and solid residue. This task will be archived by using engineering and experimental analysis which includes; pyrolysis, co-pyrolysis, and ball milling as the presence of shale oil is expected to have an influence and perhaps even increase the quality of the pyrolysis oil produced.

Currently, there are problems with the oil produced by the pyrolysis of biomass. Bio-oil gotten from the pyrolysis of biomass has a heating value range between 13-26 MJ/kg when compared to other conventional fuel oil due to its high water content [7]. Also, there a problem of energy sustainability, with the world's current consumption of electricity and demand for constant energy, there is a demand for more research in the development of an alternative and more sustainable energy source. This gives biomass an edge as it is a sustainable resource [1]. Finally, there is currently a lack of engineering research and development on the co-pyrolysis of oil shale and biomass blends even when the thermal conversion process of kerogen to bitumen in oil shale occurs at almost the same temperature range as the decomposition of biomass [8].

From previous studies, several works have been reported on the co-pyrolysis between other types of fuels [9]. Also, some research has been done on individual pyrolysis of oil shale and biomass both very few on the co-pyrolysis of both [9]. Therefore, the current study is motivated due to the abundance of oil shale and biomass in Estonia, and a drive towards a more sustainable utilization of oil shale.

The aim and objective of this research is to investigate the co-pyrolysis behavior of oil shale and biomass with the focus on the characterization of oil/tar and solid residue. In the beginning, research will be done to check the different and current techniques, methods, and technologies available. Then, engineering an effective method to obtain the desired solution having studied previous methods. An extensive experimental analysis that includes co-pyrolysis processes of oil shale and biomass to engineer a pyrolysis oil/tar with an expected high heating value, characterize the final pyrolysis products (oil/tar and solid residue).

This thesis will consist of 5 chapters.
Chapter 1: This provides an overall introduction of the thesis which includes the motivation and the objectives this thesis aims to achieve.

Chapter 2: This contains literature review on observation and analysis of previous works or studies related to the objectives of this thesis as this will help to justify the aim and objectives of this thesis.

Chapter 3: This contains the methodology of the thesis. Selection of the best engineering and experimental analysis method which would be used to achieve the aim and objectives of this thesis. Furthermore, this also provides a detailed explanation of the experimental and engineering analyses involved in the thesis.

Chapter 4: This contains detailed results and explanation of the carried-out methodology, which includes thermographs analysis, characterization Figures, and concertation tables from the engineering and experimental analysis.

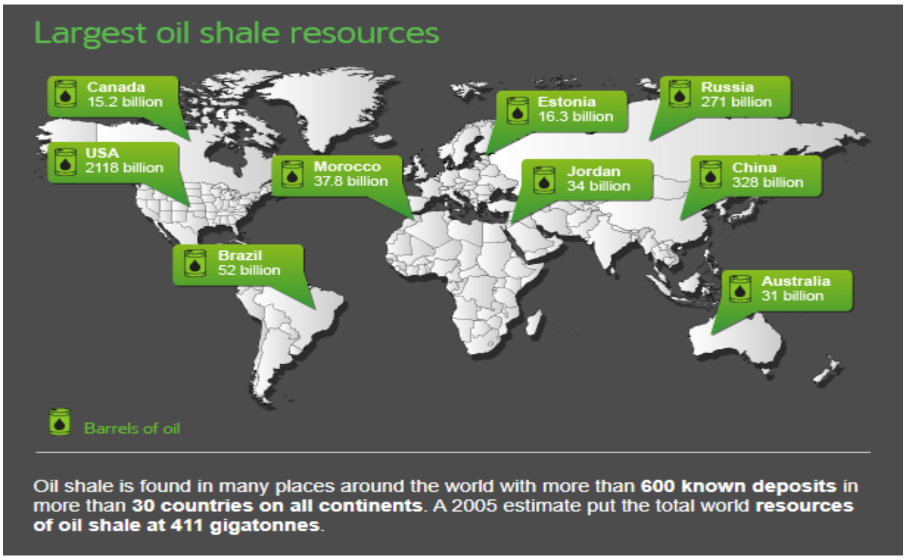
Chapter 5: This would provide the concluding part of the thesis which discusses in detail the limitation of the thesis, justification of the thesis, and suggestions for future research and development that relate to the objectives of this thesis.

2. LITERATURE REVIEW AND BACKGROUND

2.1 Background Study on Materials

2.1.1 Oil Shale

Oil shale is a sedimentary rock that contains a large amount of organic matter such as kerogen and bitumen propagated in its inorganic matrix, that yield significant amounts of shale oil upon pyrolysis. The organic matter in oil shale is kerogen which varies in its form or composition from deposit to deposit across the world. Oil shale is considered as one of the major substitute energy resources for petroleum due to its large reserves [10], [11]. Oil shale can be found across over 30 countries around the world. Estonia is the eighth country with a volume of oil shale resources at 16.3 billion barrels as can be seen in Figure 2.1 [11]. The primary products of produced by oil shale pyrolysis include semi-coke, pyrolysis water, shale gas, and shale oil. Shale oil produced by oil shale having a calorific range of 36-40 MJ/kg [12].



Largest oil shale resources

Oil shale is found in many places around the world with more than **600 known deposits** in more than **30 countries on all continents**. A 2005 estimate put the total world **resources of oil shale at 411 gigatonnes**.

Figure 2.1 Oil Shale Resources around the world [13]

2.1.2 Biomass

Biomass is a renewable organic material that comes from organic matter like plants and animals. It is a complex biogenic mass that consists of cellulose, hemicellulose, lignin, and extraneous compounds [13]. This biomass can be used as fuel for a more renewable and sustainable source of energy used to create electricity or other forms of power developed from organic materials[14]. Biomass can be harnessed from any part of the world due to its abundance, which is especially attractive for countries like Estonia, a country rich in forest land with over 50.6% of its land covered with forest [15]–[18]. The primary products of biomass pyrolysis include biochar, syngas, and bio-oil. Due to the high-water content in biomass, the bio-oil gotten from the pyrolysis of biomass has a heating value range below 26 MJ/kg when compared to other conventional fuel oil with a range of 13-26 MJ/kg [7], [19]–[23].

2.2 Pyrolysis

Pyrolysis is a thermal degradation process of organic materials at elevated temperatures in the absence of oxygen. This is an irreversible process that typically occurs at temperatures above 430 °C. Pyrolysis processes are used to convert organic materials into solid residues which consist of carbon and ash, and quantities of liquid and gas [24], [25]. However, the purpose of oil shale pyrolysis is to convert as much organic matter into liquid as possible. The yield of the oil depends on temperature, the higher the temperature, the higher is the yield of gaseous products. For the current study, the objective is to obtain non-condensable gases, liquid products, and solid char from the feedstock that would be processed through pyrolysis.

2.2.1 The effect of $CaCO_3$ on pyrolysis

Oil shale contains about 70% of mineral matter. A significant part of this mineral matter is $CaCO_3$. And this plays a significant effect on its products. A study done by Eilhann E.Kwon et al [26] on the effects of calcium carbonate on pyrolysis of sewage sludge observed that $CaCO_3$ influenced the final pyrolytic product gotten from the sewage sludge. The study showed a decrease in the yield of solid content of the pyrolytic product and an increase in the yield of liquid and gas content. Also, in another study done by Liu Hui-jun et al [27] on the effects of Ca-based additives on behaviors of slow and fast coal pyrolysis. The study showed the effect of Ca-based additives, $CaCO_3$ and $Ca(OH)_2$ on both slow pyrolysis and fast pyrolysis of coal, which lead to a slight reduction in the yield of the tar content, with a slight increase in the yields of char and gaseous product.

2.2.2 Products of Pyrolysis

The primary products of pyrolysis include solid, liquid, and gas depending on the pyrolysis process used. Most projects done by pyrolysis processes have a major interest in the liquid product due to its high energy density and has potential value as an alternative energy source to other fossil fuels like crude oil [28].

2.3 Co-Pyrolysis

Naturally, oil produced by pyrolysis of biomass contains a high level of oxygen, which reduces the caloric value of the oil. Upgrading the oil will involve the use of a catalyst, high amount of hydrogen, and a solvent which incur additional cost of the process making it more expensive than the cost of the oil itself. Having said this, co-pyrolysis offers a simple and effective method of producing high-grade pyrolytic oil [29].

Co-pyrolysis is the thermal degradation of two or more materials used as feedstock. Studies show that the use of the co-pyrolysis process has resulted in improved oil characteristics of pyrolysis oil, i.e due to co-pyrolysis, there was an increase in the oil yield, reduction of water content in the oil, and an increase in the caloric value of the oil produced [30]. For the current study, the objective is to investigate the co-pyrolysis behavior of oil shale and biomass, as the presence of shale oil is expected to have an influence and perhaps even increase the quality of the pyrolysis oil produced, and this would be processed through co-pyrolysis.

2.3.1 Mechanism of the co-pyrolysis process

Co-pyrolysis and pyrolysis have a similar mechanism, as both processes are done in a reactor at elevated temperature in the absence of air. However, for the production of oil, there are three basic steps involved:

- Preparation of feedstock: Prior to co-pyrolysis, the feedstock to be processed should to dried and ground. Drying the feedstock is essential in removing the moisture content of the feedstock as suggested by Bridgwater [31] that the moisture content of the dried feedstock should be 10%. Drying of the feedstock provides a seamless grinding process, to achieve high biomass heating rate the grounded size of the feedstock should be in particle form, having sizes less than 2-3 mm [29].
- Co-pyrolysis: The general thermal degradation temperature used in co-pyrolysis is within the range of 400-600 ^{o}C to maximize the production of oil. Within this temperature range, more than 45 wt% can be produced. Studies show that the use of inert gases during the co-pyrolysis process of the feedstock has positive effect on the liquid yield [29], [32] and nitrogen (N_2) is commonly used due to its availability and low price compared to others. The use of inert gases however depends on the type of reactor used for the co-pyrolysis process. It is important to note that co-

pyrolysis processes are influenced by different parameters ranging from the type of feedstock, heating rate, temperature, particle size, and reaction time [29].

- Condensation: This is an important process for the production of pyrolysis oil, as without condensation only char and gas products would be obtained from the process. The condensation unit coverts the physical state of the vapor generated during the process into liquid state. Studies show that rapid cooling of the vapor generated during the co-pyrolysis process is required to produce high liquid yield. [29].

2.3.2 Co-pyrolysis methods

The review of co-pyrolysis studies and method was essential in this thesis work, as it helped to generate the idea of the topic "studies on the co-pyrolysis of oil shale and biomass" in order to produce high-grade pyrolysis oil. Most of the reviewed studies were on the co-pyrolysis of biomass and waste materials with emphasis on the production of pyrolysis oil, these reviews can be seen below.

2.3.2.1 Co-pyrolysis of biomass and plastics

A study was done by Abnisa et al [33] on the co-pyrolysis of palm shell and polystyrene to obtain a high-grade pyrolysis oil. The study attempted to demonstrate a method by which high-grade pyrolysis oil can be produced by utilizing the use of biomass wastes. The investigation was carried out in Malaysia where the biomass used for this study was Palm shell. At the time of the study, palm shell waste generated in Malaysia was huge, an amount of 5.2 Mt was produced in 2009, also polystyrene generated an annual number of wastes of over 280,000 Tons in Malaysia. From the results shown, pyrolysis of the palm shell gave an oil yield of about 46.13 wt %. But when mixing the palm shell with polystyrene with the same weight ratio, the yield of oil increased to about 61.63%. The high heating value (HHV) of the oil produced by the pyrolysis of the palm shell gave a value of about 11.94 MJ/kg, while the high heating value of the oil produced by the co-pyrolysis of palm shell with polystyrene gave a value of about 38.01 MJ/kg. The above result was gotten under the following conditions; the temperature was set at 500 ^{o}C with a heating rate of 10 ^{o}C, a reaction time of 60 min, and an inert gas (N_2) flow rate of 2 L/min. However, it is important to note that the quality of the oil was improved by the addition of polystyrene during pyrolysis also, the experiment was performed without any solvents, catalysts, or additional pressure.

2.3.2.2 Co-pyrolysis of biomass and waste tires

A study was done by Q. Cao et al [34] on the investigations into the characteristics of oils produced from co-pyrolysis of biomass and tire. For this study, sawdust powder with a particle size ranging from 198–350 μm was mixed with waste tire which was grounded to powder size with a particle size of less than 165 μm. The ratios of the sawdust to waste tire mass in the feedstock varied at 0:100, 40:60, 60:40, and 100:0. From the results shown, the oil yield achieved was 45.0 wt%, 46.2 wt%, 47.0 wt%, and 47.2 wt% according to the respective feedstock ratio and the waste tire mass contribute to 0%, 40%, 60%, and 100% of the mixture of the oil yield respectively. The high heating value (HHV) of the oil produced by the pyrolysis of the sawdust gave a value of about 28.51 MJ/kg, while the high heating value of the oil produced by the co-pyrolysis of sawdust with waste tire mass gave a value of about 42.44 MJ/kg. The above result was gotten under the following conditions; fixed-bed pyrolysis reactor was used, before heating, nitrogen was blown into the reactor for 30 min, the temperature was set at 500 ^{o}C with a heating rate of 20 ^{o}C, a reaction time of minimum of 3.5 hours. It is important to note that the quality of the oil was improved by the addition of waste tire mass during pyrolysis also, the experiment was performed with a catalyst of such as 10 g of Santa Barbara Amorphous-15 (SBA-15), Mobil Composition of Matter No. 41 (MCM-41) or Zeolite Socony Mobil No. 5 (HZSM-5).

2.3.2.3 Co-pyrolysis of oil shale and plastics

For this study, Aboulkas et al [35] aim was to maximize the oil yield from the pyrolysis process. Three plastic materials: low density polyethylene (LDPE), polypropylene (PP), and high density polyethylene (HDPE) were used alongside oil shale. The experiment was carried out in a stainless steel autoclave in the presence of nitrogen. From the result shown, co-pyrolysis process lead to an increase in the oil yield when compared to individual pyrolysis. The most oil yield was produced at a temperature range of 500-525 ^{o}C, at a heating rate of 10 ^{o}C. However, the high heating value (HHV) of the oil produced was not accounted for in this study as well as the characterization of tar.

2.3.2.4 Co-pyrolysis of oil shale and wheat straw

This study was carried out by Bin Chen et al [36] in closed-system pyrolysis with a fixed bed reactor and an open-system with a thermogravimetry–mass spectrometry (TG–MS) analyzer. From the results gotten, it was observed that oil shale played a vital role in the distribution of gas contents during the co-pyrolysis process, it was also observed that ratio blend affected the final pyrolytic product, for example, when there was an increase in wheat straw content, the gas and water yields increased, while the oil and semicoke decreased.

Table 2.1 Comparison of thermal decomposition methods

Category	**Characteristic**	**Advantages**	**Disadvantages**
Pyrolysis	Thermal degradation of a single feedstock at elevated temperature in the absence of air.	The feedstock is converted to energy.	The quality of the final pyrolytic product is solely dependent on the single feedstock. This is an irreversible process. Catalyst is used to improve the quality of the final pyrrolic product which adds to the running cost.
Co-pyrolysis	Thermal degradation of two or more feedstock at elevated temperature in the absence of air.	Feedstocks are converted to energy. Increase in the oil yield and quality of oil as well as the increase in the quality of the final pyrrolic products. Shown promise for future application in industry because of its attractive performance/cost ratios.	This is an irreversible process. Some char and ash produced by this process are sometimes toxic which could be a dangerous waste to the environment if not properly disposed of.

2.3.3 Synergistic effects of feedstock used in co-pyrolysis

The major factor for the improvement of the pyrolytic product produced by co-pyrolysis is the synergistic effect between the feedstocks. However, the common synergistic effects of co-pyrolysis are discussed below.

2.3.3.1 Mechanism of synergistic effects

To date, there are ongoing research to study the synergistic effect of feedstock used during co-pyrolysis. These effects depend on factors ranging from the type of catalyst, type of component, reaction time, heating rate, temperature, the addition of a catalyst, and hydrogen donor [37], [38]. With all the above factors, blending of the feedstock plays a major role in the synergistic effect thus complicatedly varying the negative or positive synergy effect [39].

2.3.3.2 Oil yield

As seen from previously reviewed studies, the co-pyrolysis process has the propensity to increase the oil yield produced from the feedstock during the process. There might be many factors behind this, however, biomass plays a major role due to the composition of biomass. It is possible to predict the amount of liquid content that would be produced when the composition of the biomass is measured. Proximate analysis helps to measure the content of biomass in four different constituents: moisture content, fixed carbon, volatile matter, and ash content [40]. Studies show that the main factors that have an effect on the production of oil yield are the ash content and volatile matter. A study by Asadullah et al [41] showed that volatile matter is usually converted to bio-oil during condensation, and also Omar et al [42] discovered that a high volatile content gives the benefits of high volatility and reactivity, which are ideal for fluid fuel creation. Volatile matter is a major factor in producing pyrolysis oil, and to maximize the advantage of volatile matter, the co-pyrolysis process needs to be done under controlled environment and conditions. An investigation done by Paethanom et al [43] where co-pyrolyisis operation was done at three different temperatures 600, 800, and 1000 ^{o}C, it was observed that at 600 ^{o}C, the highest volatile matter was produced, and at the higher temperatures high fixed carbon contents were produced.

2.3.3.3 Quality of Oil

The improvement of the quality of pyrolysis oil is also as a result of the synergistic effect between the feedstocks. From the reviewed work above [33], [34], it can be seen that there was a significant increase in the calorific value/heating value of the oil produced by co-pyrolysis when compared to the bio-oil from single pyrolysis, this is as a result of the low heating value of most wood-based biomass.

2.3.3.4 Quality of char

The increase in the heating value of char produced by the co-pyrolysis process is also as a result of the synergistic effect. Paradela et al [44] observed that solid content gotten from the co-pyrolysis of waste plastic and biomass had a higher heating value when compared to some coal types. Also, a similar result was observed in the study by Brebu et al [45] where the char produced by co-pyrolysis of pinecone and synthetic polymer had a higher caloric value when compared to the heating value of char produced by the pyrolysis of pinecone.

3. METHODOLOGY

This chapter contains the methodology of the thesis. Selection of the best engineering and experimental analysis method which would be used to achieve the aim and objectives of this thesis. Furthermore, this also provides a detailed explanation of the experimental and engineering analyses involved in the thesis.

3.1 Materials

3.1.1 Oil shale

Oil shale as earlier stated has large deposits around the world, and since this present study is in Estonia, the oil shale used for this thesis is Kukersite oil shale. Table 3.1 shows the elemental (chemical) composition of the oil shale used.

Table 3.1 Chemical composition of Oil shale

Ash in dry oil shale	Calorific value MJ/kg	Elemental composition				
		C	H	N	O	S
51,62%	9.01	26.03%	2.46%	0.06%	18.08%	1.75%

The preparation of the oil shale feedstock was done after the chemical composition was known. The oil shale feedstock was first of all crushed to small particle sizes of 180 µm, thereafter, it was ball-milled at 200 revolutions per minute (RPM) for 10 minutes to get a fine powder particle size of the feedstock that would be used for the experiment.

3.1.2 Biomass

The biomass used for the present study is black alder. Black and grey alder make up 4% of Estonian tree forest area distribution and its availability in Estonia is quite common, thereby making it the choice of the biomass feedstock for the current study [46]. Table 3.2 shows the elemental (chemical) composition of the biomass used.

Table 3.2 Chemical composition of Biomass

Higher Heating Value (HHV) MJ/kg	Lower Heating Value (HHV) MJ/kg	Elemental composition				
		C	H	N	O	S
20.00	18.64	50.47%	6.55%	0.231%	42.699%	-<0.05%

The preparation of the feedstock for the biomass was done in two stages. First, it was crushed into smaller particle sizes between 0.25 and 0.5 mm, thereafter, it was ball-milled at 200 revolutions per minute (RPM) for 10 minutes to get a fine powder particle size that would be used for the experiment.

3.2 The Mixture Ratio of the Feedstock

The co-pyrolysis process was to be done in 5 different ratios. This was done so that we could study the behavior as well as the synergistic effect of feedstock in the different ratios. The ratios of the oil shale to the biomass in the feedstock varied at 0:100, 50:50, 30:70, 70:30, and 100:0. In other to achieve a prefecture mixture in ratios, the two feedstock at the 3 different ratios were ball-milled together to get a fine powder particle size that would be used for the co-pyrolysis process.

3.3 Experimental Apparatus and Procedure

The current study aims at studying the co-pyrolysis behavior of oil shale and biomass, and to achieve this, two methods were chosen that would help show these interactive behaviors as well the synergistic effect of feedstock used during the co-pyrolysis process. Thermogravimetric analysis (TGA) and Fischer assay (FA) are the two methods that would be used for the current study.

3.3.1 Thermogravimetric analysis (TGA)

In order to study and understand the pyrolysis behavior of oil shale and biomass as well as the co-pyrolysis behavior of oil shale and biomass, we need to know how the mass will change with respect to the rise in temperature.

Thermogravimetric analysis (TGA) is an analytical tool used to study and understand thermal events with respect to the weight change that occurs at a constant or a given heating rate. The DuPont instruments 951 thermogravimetric analyzer was used to determine the mass loss percentage of the feedstock during pyrolysis and co-pyrolysis processes.

Figure 3.1 DuPont instruments 951 thermogravimetric analyzer

The TGA used for the current study was not automated, as a result of this, other devices such as a mass flow controller (Alicat Scientific Inc) which helps to control the flow of nitrogen gas (N_2), and an automated temperature controller (Cole–Parmer Digi-Sense) was integrated into the experimental system. Signals from the TGA were collected as data with a USB 6210 data acquisition card (National Instruments) and recorded using a special program created on Labview 8.0 for recording the data. With all these additions to the experimental system, the whole TGA process became fully automated.

The feedstocks, having fine powder particle size for the pyrolysis as well as the co-pyrolysis process were put into a sample pan which is made of Aluminium oxide (Al_2O_3) and then placed into the TGA on a quartz balanc. The mass of the feedstock ranged from 11 to 13 mg.

All thermogravimetric experiments across all 5 ratios were carried out under the same conditions. The Nitrogen gas (N_2) flow rate was set at 100 ml/min, and a constant heating rate of 10 °C/min from 60 ^{o}C to 520 ^{o}C (Figure 3.2).

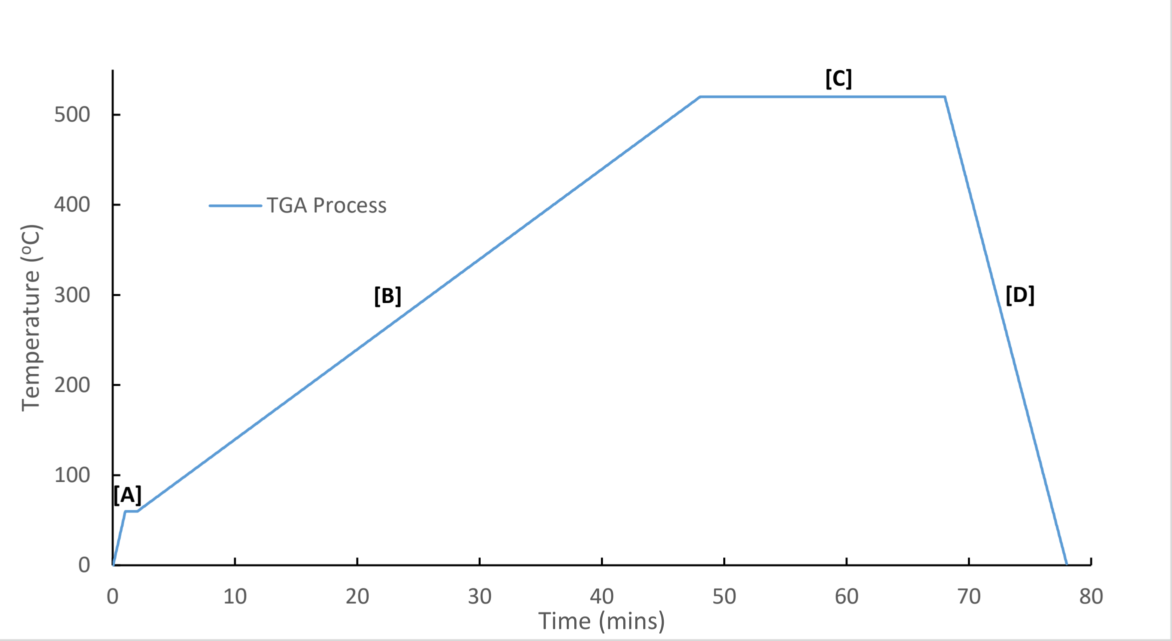


Figure 3.2 TGA heating program

The whole thermogravimetric heating process was divided into 5 segments with a total analysis time of 68 minutes. In the first segment, the feedstock was heated to 60 °C in 1 minute, this process was held isothermally for 1 minute (segment 2), thereafter the feedstock was heated to 520 °C for 46 minutes (segment 3) and was held isothermally at 520 °C for 20 minutes (segment 4) before cooling down (segment 5) as can be seen in Figure 3.2. Zones A and C are isothermal segments, while Zone B is heating and zone D is cooling.

Three thermocouples were installed in the TGA, all three were close to the sample pan, however, the one closest to the sample pan was used as the reference in the thermogravimetric experiment carried out. The repeatability of the thermogravimetric experiments was good, as each ratio of feedstock was conducted twice and had very similar results and mass loss curves. (Chapter 4.1.1)

3.3.2 Fischer Assay (FA)

The oil yield, as well as the quality of pyrolysis oil, is one of the important objectives of the current study. Fischer assay is old but still a very effective laboratory test in determining the oil yield as well as the water, gas, and solid residue produced from oil shale as well as any solid organic material.

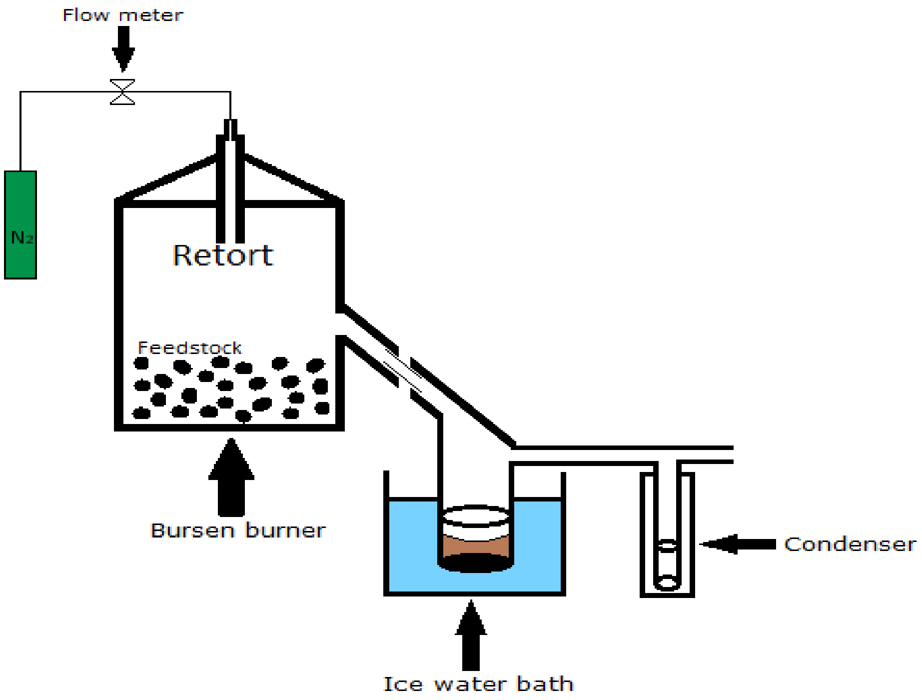


Figure 3.3 Fischer assay setup

The Fischer assay setup for the current study was modified and completely manual. The setup consisted of a retort, bunsen burner, a thermocouple, a mass flow controller (Alicat Scientific Inc), which helps to control the flow of nitrogen gas (N_2), a round-bottom flask, a cooling bath, a U-tube, and a condenser. The current study was primarily focused on pyrolysis liquid, so the gaseous pyrolysis by-product was not taken into consideration.

The feedstock, having fine powder particle size for the pyrolysis as well as the co-pyrolysis process was put into the Fischer assay retort. The mass of the feedstock was 30 g. The Fischer assay retort was subject to nitrogen gas (N_2), which was introduced through the tube positioned at the top of the lid of the retort.

All the Fischer assay experiments across all 5 ratios were carried out under the same conditions. The Nitrogen gas (N_2) flow rate was set at 10 ml/min, and a constant heating rate of 10 °C/min. Nitrogen gas (N_2) was flushed into the system for 25 minutes before the start of every experiment.

The whole Fischer assay heating process took 87 minutes. The retort was heated up to 500 °C at 10 °C/min for 47 minutes, thereafter, slow heating from 500°C to 520°C for 20 minutes and then held isothermally at 520°C for 20 minutes. The repeatability of the Fischer assay experiments was good, as each ratio of feedstock was conducted twice and had very similar results in oil yield and mass loss. (Chapter 4.1.2)

4. RESULTS AND DISCUSSION

4.1 Mass Loss

Both methods carried out in the study of the co-pyrolysis of oil shale and biomass showed significant mass loss across the different 5 ratios. Mass loss across the two methods was calculated using the following equation, (4.1) and (4.2).

$$Mass\ loss\ = F_i - \ F_f \qquad \textbf{(4.1)}$$

$$Mass\ loss\ [\%] = \frac{F_i - F_f}{F_i} * 100 \qquad \textbf{(4.2)}$$

Where F_i is the initial weight of the feedstock and F_f is the final weight of the char/semicoke gotten after pyrolysis and co-pyrolysis.

4.1.1 Mass loss in TGA process

Below are the results tabular (Table 4.1) and graphical representation (Figure 4.1) of the mass loss recorded during the TGA process.

Table 4.1 Mass loss in TGA process

Feedstock Ratio	Temperature (°C)	Heating rate (°C/min)	F_i (mg)	F_f (mg)	Mass loss (mg)	Mass loss (%)
100% OS	520	10	12.5750	9.4941	3.0809	24.50
100% BM	520	10	11.7572	2.6818	9.0754	77.19
30% OS 70% BM	520	10	12.1186	4.3726	7.7460	63.92
50% OS 50% BM	520	10	12.0493	5.7632	6.2861	52.17
70% OS 30% BM	520	10	12.8597	7.3491	5.5106	42.85

In the TGA process, the pyrolysis of each ratio was carried out twice, and since repeatability was achieved, the average result of the runs was recorded. Table 4.1 above represents the average results of the two runs in each ratio. The mean and the standard deviation on the runs can be seen in Table 4.2.

Table 4.2 Mean and standard deviation of the TGA mass loss results

Feedstock Ratio	Mean (mg)	Standard Deviation (mg)
100% OS	3.0809	0.1576
100% BM	9.0754	0.5817
30% OS 70% BM	7.7460	0.4583
50% OS 50% BM	6.2861	0.0867
70% OS 30% BM	5.5106	0.1920

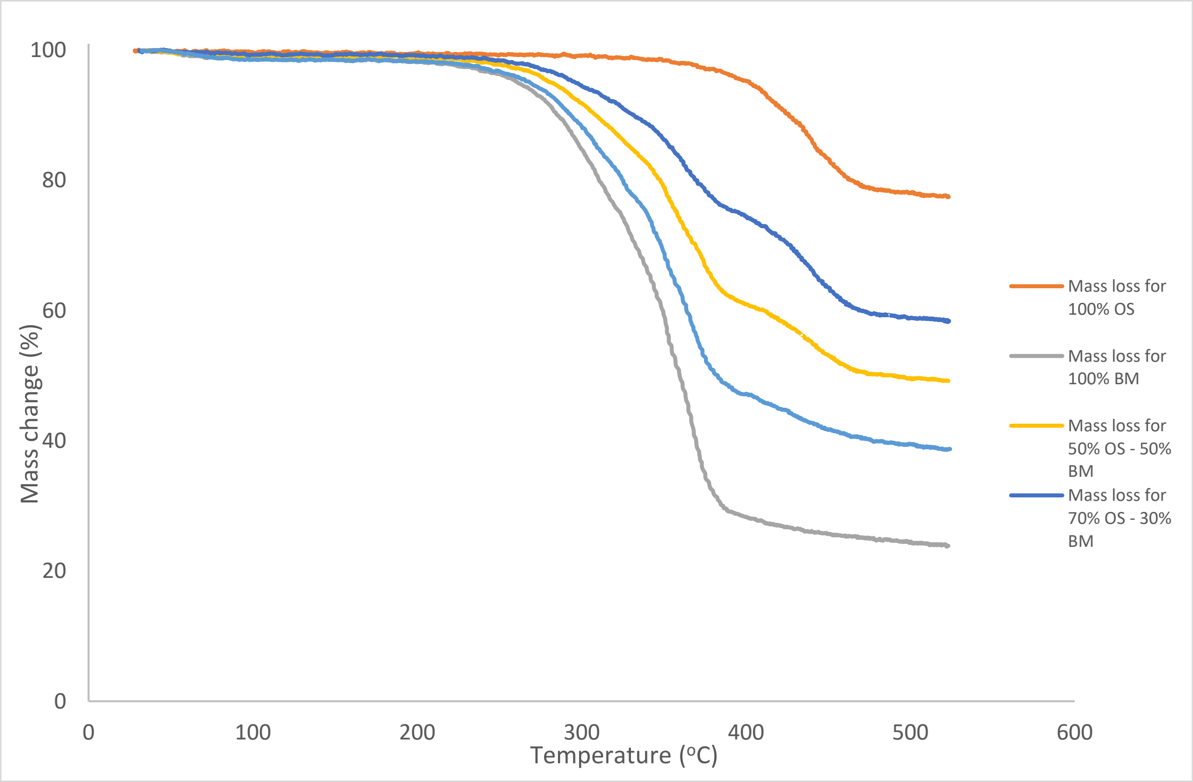


Figure 4.1 Mass loss percentage in TGA process

From Table 4.1 and Figure 4.1, it can be seen that there was significant mass loss across all ratios. Ratio 0:100 (100% OS) had the lowest mass loss at 24.50% due to its natural low water and organic content. Decomposition can be seen to have started at 320 ºC for this ratio. After the thermal decomposition of the 100% OS feedstock, a black-colored char was left on the sample pan. Ratio 100:0 (100% BM) had the highest mass loss at 77.19%, this was an expected result as biomass is generally known for its high water content, the high water content of bio-oil derives from water in the feedstock and dehydration reactions during biomass pyrolysis [47]. However, the biomass feedstock used for the current study was dried making the water content quite low, so we can attribute the drastic mass loss to the thermal decomposition of its organic compounds such as cellulose, hemicellulose, and lignin. Biomass generally has more organic content as compared to oil shale. The decomposition for 100% BM could be noticed to have started at 220 °C. After the thermal decomposition of the 100% BM feedstock, black-colored biochar was left on the sample pan.

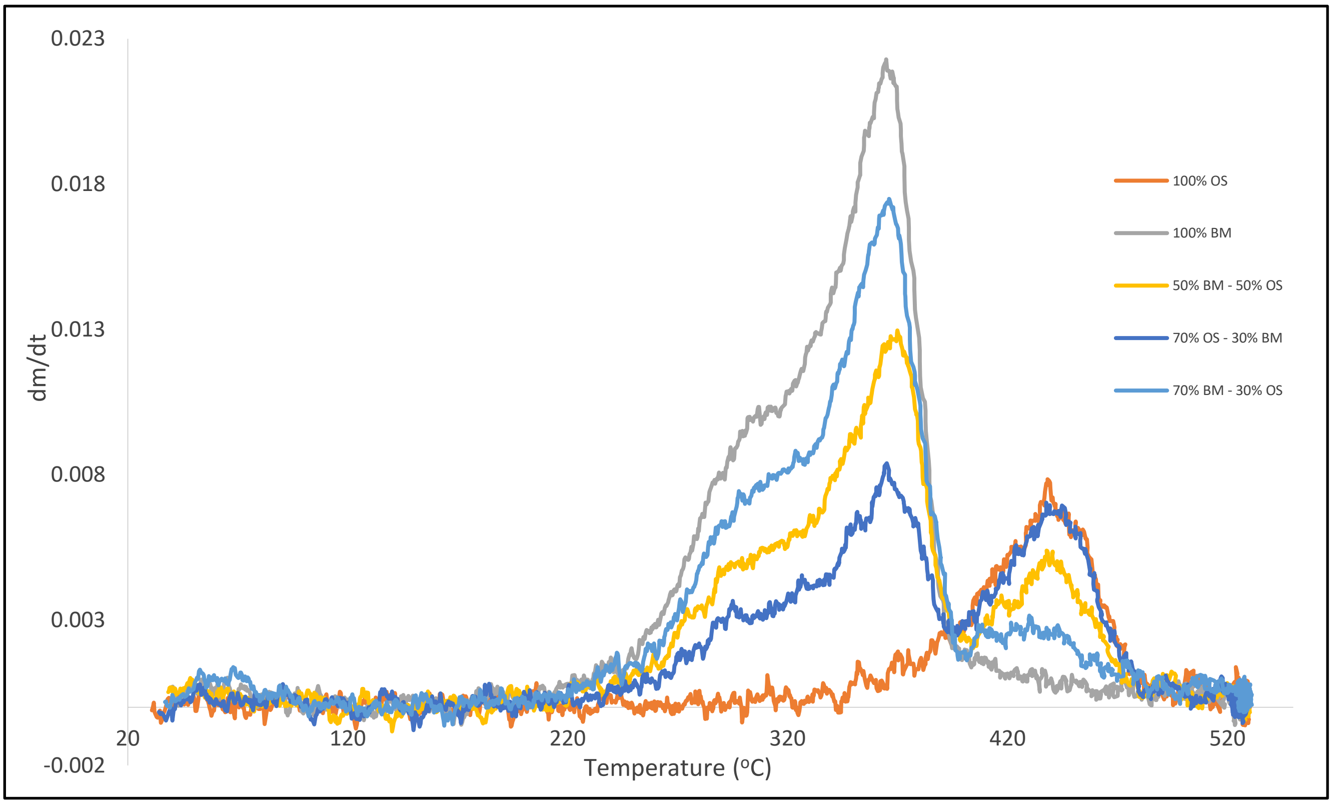


Figure 4.2 dm/dt graph of mass loss in TGA process

Figure 4.2 best helps us to understand the mass loss with respect to the rise in temperature. The y-axis represents the differential in mass over time. We could see that the decomposition of the 3 mixed ratios 50:50, 30:70, and 70:30 happened in two phases as the major decomposition occurred in the temperature range of 200-500 °C. The first phase was the thermal decomposition of biomass with respect to its content of the ratio of the mixed feedstock, as we can see that there was more biomass thermal decomposition in the 70% BM 30% OS feedstock mixture as compared to the biomass thermal decomposition of 30% OS 70% BM feedstock ratio. In the second phase of the thermal decomposition, oil shale decomposed with respect to its content of the ratio of the mixed feedstock. In ratios that had more oil shale content, we could see that the final stage of the thermal decomposition took place with the oil shale feedstock ratio. TGA analysis was ended at 520 °C.

Table 4.3 Calculated results against experimental results of mass loss in TGA process

Feedstock Ratio	Calculated results (mg)	Experimental results (mg)	Difference
100% OS	-	3.0809	-
100% BM	-	9.0758	-
30% OS 70% BM	7.4388	7.7460	-0.3072
50% OS 50% BM	6.1265	6.2861	-0.1596
70% OS 30% BM	5.1834	5.5106	-0.3272

Table 4.3 shows the calculated result and the experimental result of mass loss during the TGA process. The experimental results are based on the results gotten during the TGA process while the calculated results are from the calculation of the mixed mass loss ratio of the feedstock by the individual mass loss ratio of the two feedstock. From Table 4.3 we can see that the experimental results and the calculated results were quite similar however the experimental result recorded higher mass losses, this could be as a result of some imperfection in the mixed feedstock ratios and also the uncertainty of the individual feedstock, i.e 100% OS and 100% BM effect on the mixed ratio.

4.1.2 Mass loss in Fischer Assay process

Pyrolysis, as well as co-pyrolysis of the feedstock ratios, took place in a modified Fischer assay retort. Table 4.4 represents the mass recorded during the process. The mean and the standard deviation on the runs can be seen in Table 4.5.

Table 4.4 Mass loss in Fischer assay process

Feedstock Ratio	Temperature (°C)	Heating rate (°C/min)	F_i (g)	F_f (g)	Mass loss (g)	Mass loss (%)
100% OS	520	10	30	21.92	8.08	26.93
100% BM	520	10	30	7.83	22.17	73.90
30% OS 70% BM	520	10	30	12.50	17.50	58.35
50% OS 50% BM	520	10	30	14.96	15.04	50.13
70% OS 30% BM	520	10	30	17.94	12.06	40.20

In the Fischer assay process, the pyrolysis of each ratio was carried out twice, and since repeatability was achieved, an average result of the runs was done. Table 4.5 above represents the average results of the two runs in each ratio.

Table 4.5 Mean and standard deviation of the Fischer assay mass loss results

Feedstock Ratio	Mean (g)	Standard Deviation (g)
100% OS	8.08	0.06
100% BM	22.17	0.37
30% OS 70% BM	17.51	0.12
50% OS 50% BM	15.04	0.75
70% OS 30% BM	12.06	0.20

Table 4.6 Calculated results against experimental results of mass loss in Fischer assay

Feedstock Ratio	Calculated results (g)	Experimental results (g)	Difference
100% OS	-	8.08	-
100% BM	-	22.17	-
30% OS 70% BM	17.94	17.51	0.43
50% OS 50% BM	15.13	15.04	0.25
70% OS 30% BM	12.31	12.06	0.43

Table 4.6 shows the calculated result and the experimental result of mass loss during the Fischer assay process. The experimental results are based on the results gotten during the Fischer assay process while the calculated results are from the calculation of the mixed mass loss ratio of the feedstock by the individual mass loss ratio of the two feedstock. From Table 4.6 we can see that the experimental results and the calculated results were quite similar, however, the calculated result recorded higher mass losses, this could be as a result of the uncertainty of the individual feedstock, i.e 100% OS and 100% BM effect on the mixed ratio as well as human error as the Fischer assay method used in the current study was mainly controlled manually.

It can be observed that both methods used for the current study of co-pyrolysis behavior of oil shale and biomass, had similar mass loss percentages. From Table 4.7, the final results when compared showed that biomass had the highest mass loss percentage among the ratios and oil shale had the lowest, it was interesting to see its influence in the 3 different ratios mass loss percentages observed across both methods. As the ratio with high biomass to oil shale content had more mass loss percentage compared to the ratio with high oil shale to biomass content.

Table 4.7 Comparison between mass loss percentage in TGA and Fischer assay

S/N	Experiment Type	Feedstock Ratio	Mass Loss Percentage (%)
1	TGA	100% Oil Shale	24.14%
	Fischer Assay		26.93%
2	TGA	100% Biomass	77.19%
	Fischer Assay		73.90%
3	TGA	30% Oil Shale 70% Biomass	63.92%
	Fischer Assay		58.35%
4	TGA	50% Biomass 50% Oil Shale	52.17%
	Fischer Assay		50.13%
5	TGA	70% Oil Shale 30% Biomass	42.85%
	Fischer Assay		40.20%

The TGA process generally recorded more mass loss percentage when compared to the Fischer assay process, this could be as a result of the TGA heating process is fully automated as compared to the Fischer assay heating process which is controlled manually with the bunsen burner. Also, the mass of the feedstock used for the TGA was smaller in mass when compared to the mass of the feedstock used for the Fischer assay. Therefore, the pyrolysis of the feedstock in the Fischer assay process would have higher residual content in the char than that of TGA.

4.2 Product Yields

4.2.1 Pyrolytic liquid (oil+water) yield

The pyrolysis liquid analyzed in the current study was obtained in Fischer assay experiments. The liquid yield was measured by first weighing the round-bottom flask before the experiment was conducted and after the experiment was finished it was reweighed to get the mass of the pyrolysis liquid produced. The liquid yield was calculated using the following equation (4.3). Table 4.8 represents the liquid yield produced from the Fischer assay for the current study.

$$Oil\ yield\ [\%] = \frac{F_o}{F_i} * 100 \qquad \textbf{(4.3)}$$

Where F_i is the initial weight of the feedstock and F_o is the weight of the liquid after pyrolysis and co-pyrolysis of the feedstock.

Table 4.8 Liquid yield from Fischer assay

Feedstock Ratio	Temperature (°C)	Heating rate (°C/min)	F_i (g)	Liquid yield	
				F_o (g)	(%)
100% OS	520	10	30	6.42	21.38
100% BM	520	10	30	12.64	42.13
30% OS 70% BM	520	10	30	10.02	33.38
50% OS 50% BM	520	10	30	5.11	17.03
70% OS 30% BM	520	10	30	7.78	25.92

From Table 4.8 we see the liquid yield percentage across the different ratios. Ratio 100:0 (100% Biomass) had the highest yield compared to the ratio 0:100 (100% Oil shale) and the other mixed feedstock ratios. The liquid yield varied across the 3 mixed feedstock ratios, however, we could observe the effect of biomass content across the feedstock as the mixed ratio with the high biomass content (70% BM 30% OS) produced more yield compared to the other two mixed ratios (50% OS 50% BM & 70% OS 30% BM). It is important to note that the feedstock ratios that produced high mass loss percentages also had higher liquid yield. The color of the oils produced from the mixed ratios was dark brown having a smokey odor.

Pyrolysis water was also present in all oil produced by the Fischer assay retort, been very visible in the mixed ratios with biomass when compared to the 100% oil shale. A major reason could be the effect of the biomass feedstock. Bio oils generally have high water content usually up to 30% [48].

Table 4.9 Calculated results against experimental results of liquid yield in Fischer assay

Feedstock Ratio	Calculated results (g)	Experimental results (g)	Difference
100% OS	-	6.42	-
100% BM	-	12.64	-
30% OS 70% BM	10.77	10.02	0.75
50% OS 50% BM	9.53	5.11	4.42
70% OS 30% BM	8.28	7.78	0.50

Table 4.9 shows the calculated result and the experimental result of mass loss during the Fischer assay process. The experimental results are based on the results gotten during the Fischer assay process while the calculated results are from the calculation of the mixed liquid yield ratio of the feedstock by the individual liquid yield ratio of the two feedstock. From Table 4.9 we can see that the experimental results and the calculated results were quite similar except for the ratio of 50% OS 50% BM which showed a significant difference, this could be as a result of the influence in the interaction of the mixed feedstock on heat and mass transfer during the co-pyrolysis process. The other two mixed ratios had similarities in result, however, the calculated result had slightly higher results.

4.2.2 Char yield

Char was one of the by-products produced by the Fischer assay method. The char yield was measured by weighing the retort before the experiment and after the experiment to get the mass of the char produced. Char yield was calculated using the following equation (4.4). Table 4.10 represents the char yield produced from the Fischer assay for the current study.

$$Char\ yield\ [\%] = \frac{F_c}{F_i} * 100 \qquad \textbf{(4.4)}$$

Where F_i is the initial weight of the feedstock and F_c is the weight of the char after pyrolysis and co-pyrolysis of the feedstock.

Table 4.10 Char yield from Fischer assay

Feedstock Ratio	Temperature (°C)	Heating rate (°C/min)	F_i (g)	Char yield	
				F_c (g)	(%)
100% OS	520	10	30	21.92	73.07
100% BM	520	10	30	7.83	26.10
30% OS 70% BM	520	10	30	12.50	41.65
50% OS 50% BM	520	10	30	14.74	49.87
70% OS 30% BM	520	10	30	17.94	59.80

From Table 4.10 we see the char yield percentage across the different ratios. Ratio 100:0 (100% BM) had the lowest char yield compared to the ratio 0:100 (100% OS) and the other mixed feedstock ratios. The char yield varied across the 3 mixed feedstock ratios, however, we could observe the effect of biomass content across the feedstock as the mixed ratio with the high biomass content (70% BM 30% OS) produced less char compared to the other two mixed ratios (50% OS 50% BM & 70% OS 30% BM). After the pyrolysis and co-pyrolysis of the feedstock, the char was compact in structure taking the conical shape of the retort. The color of the char produced was dark brown.

4.2.3 Gas yield

The gas produced from the different ratios in the current study was not collected and analyzed as one of the main focuses of the current study is on the production and characterization of oil produced by the Fischer assay process. However, the amount of gas produced during the process was accounted for. The gas yield was calculated using the following equation, (4.5), (4.6), and (4.7). Table 4.11 represents the gas yield produced from the Fischer assay for the current study.

$$F_{gp} = (F_c + F_o) \tag{4.5}$$

$$Gas\ yield\ [g] = F_i - F_g \tag{4.6}$$

$$Gas\ yield\ [\%] = \frac{F_i - F_g}{F_i} * 100 \tag{4.7}$$

Where F_i is the initial weight of the feedstock and F_c is the weight of the char and F_o is the weight of the oil after pyrolysis and co-pyrolysis of the feedstock. F_{gp} is gas produced.

Table 4.11 Gas yield from Fischer assay

Feedstock Ratio	Temperature (°C)	Heating rate (°C/min)	F_i (g)	F_{gp} (g)	Gas yield	
					(g)	(%)
100% OS	520	10	30	28.34	1.66	5.53
100% BM	520	10	30	20.47	9.53	31.77
30% OS 70% BM	520	10	30	22.51	7.49	24.97
50% OS 50% BM	520	10	30	20.07	9.93	33.10
70% OS 30% BM	520	10	30	25.72	4.28	14.27

4.3 Characterization of Pyrolysis Liquid

Different detailed techniques for the characterization of the pyrolysis oils produced by the Fischer assay method in the current study were performed to reveal the effects of the co-pyrolysis of oil shale and biomass.

4.3.1 Density

The density of the pyrolysis liquid was measured with an Anton Paar DMA 5000M oscillating tube density meter. The densities reported in the current study were measured at three temperatures 15.6 °C, 20 °C, and 40 °C. The results of the density across the three different temperatures of the pyrolysis liquids are given in Table 4.12. The calculated result of the density was calculated using the density mixing equation (4.8) and the result of the calculated density against experimental density is given in Table 4.13. This equation could be used to forecast the density of a mixture.

$$Density\ mixing\ rule\ = \frac{1}{(\frac{X_o}{D_o})+(\frac{X_b}{D_b})} \tag{4.8}$$

Where X_o is the mass fraction of oil shale feedstock and D_o is the density of 100% OS of the char and X_b is the mass fraction of the biomass and D_b is the density of 100% BM.

Table 4.12 Density of pyrolysis liquid

Feedstock Ratio	Density @15.6°C(g/cm^3)	Density @20°C(g/cm^3)	Density @40°C(g/cm^3)
100% OS	0.9704	0.9672	0.9523
100% BM	1.1284	1.1242	1.1113
30% OS 70% BM	1.1282	1.1241	1.1109
50% OS 50% BM	1.1246	1.1203	1.1048
70% OS 30% BM	1.0549	1.0512	1.0348

Being that water is denser than shale oil, it was observed that the oil produced by 100% BM was denser when compared to the other pyrolysis liquid. Bio-oils are complicated oils containing emulsified water and mostly oxygen containing organic compounds which affect the density of bio-oil. The density of the bio-oil produced in the current study was similar to other bio-oil, as the density is within the range of 1.1-1.3 g/cm^3 [49]. The density of the shale oil produced was similar to that of other kukersite oil shale sample measured [50], [51] and we can see across the 3 mixed ratios the effect of biomass contents on the density, as ratios with high biomass content were denser compared to ratios that had more oil shale content. It is important to note that the analysis for each oil was repeated and repeatability was achieved in the analysis.

Table 4.13 Calculated result against the experimental result of the liquid density at 20 °C

Feedstock Ratio	Calculated results (g/cm^3)	Experimental results (g/cm^3)	Difference
100% OS	-	0.9672	-
100% BM	-	1.1242	-
30% OS 70% BM	1.088	1.1282	0.0397
50% OS 50% BM	1.066	1.1203	0.0544
70% OS 30% BM	1.033	1.0512	0.0180

From Table 4.13, we could see that equation 8 used was able to forecast the density of a mixture.

4.3.2 Refractive index

The refractive index (RI) is the measure of aromaticity and the unsaturation of a liquid. The refractive index measurement was conducted using an Anton Paar Abbemat HT refractometer at a reference temperature of 20 °C and a wavelength of 589.3 nm. The analysis of each oil was carried out repeatedly giving similar values. Table 4.14, shows the values measured.

Table 4.14 Refractive index of pyrolysis liquid

Feedstock Ratio	Refractive index @20°C (n_D)
100% OS	1.5357
100% BM	1.4297
30% OS 70% BM	1.4291
50% OS 50% BM	1.4393
70% OS 30% BM	1.4866

The refractive index and density are proportional [52]. Thus, the denser the liquid, the higher the refractive index will. Shale oil had the highest refractive index in the current study as it was mostly oil produced, while the mixed feedstock produced a lower refractive index. This could be a result of the presence of pyrolysis water in the mixed ratio liquid. Feedstock ratios with high biomass content produced more pyrolysis water and had low refractive index when compared to Feedstock ratios with high oil shale content.

4.3.3 Viscosity

The viscosity of the pyrolysis liquid was measured with an Anton Paar Modular Compact Rheometer (MCR) series. The viscosity result reported in the current study were measured at 40 °C. Table 4.15 shows the result recorded.

Table 4.15 Viscosity of pyrolysis oil

Feedstock Ratio	Viscosity @40°C(mPa.s)
100% OS	28.880
100% BM	4.854
30% OS 70% BM	4.922
50% OS 50% BM	5.266
70% OS 30% BM	9.295

We can see the effect of oil shale content on the viscosity of the liquid produced. The shale oil produced was low viscous oil having the highest viscosity amongst the pyrolysis liquid produced in the current study. Biomass had the lowest viscosity due to high water content. The viscosity of the liquid produced in the current study will play a vital role in the caloric value of the liquids. This is because the more viscous a liquid is, the stronger the intermolecular forces are. So when the liquid is heated up, the molecules have more kinetic energy and so they can more easily break free of the intermolecular forces.

4.3.4 Microscopic visual analysis

All pyrolysis oil produced during the Fischer assay was visually observed under the BRESSER Biolux digital Microscope. The oil samples were visually observed under 3 objectives, 4x, 10x, and 40x. Figures 4.3-4.7 show the microscopic images of the pyrolysis oil in its different ratios.

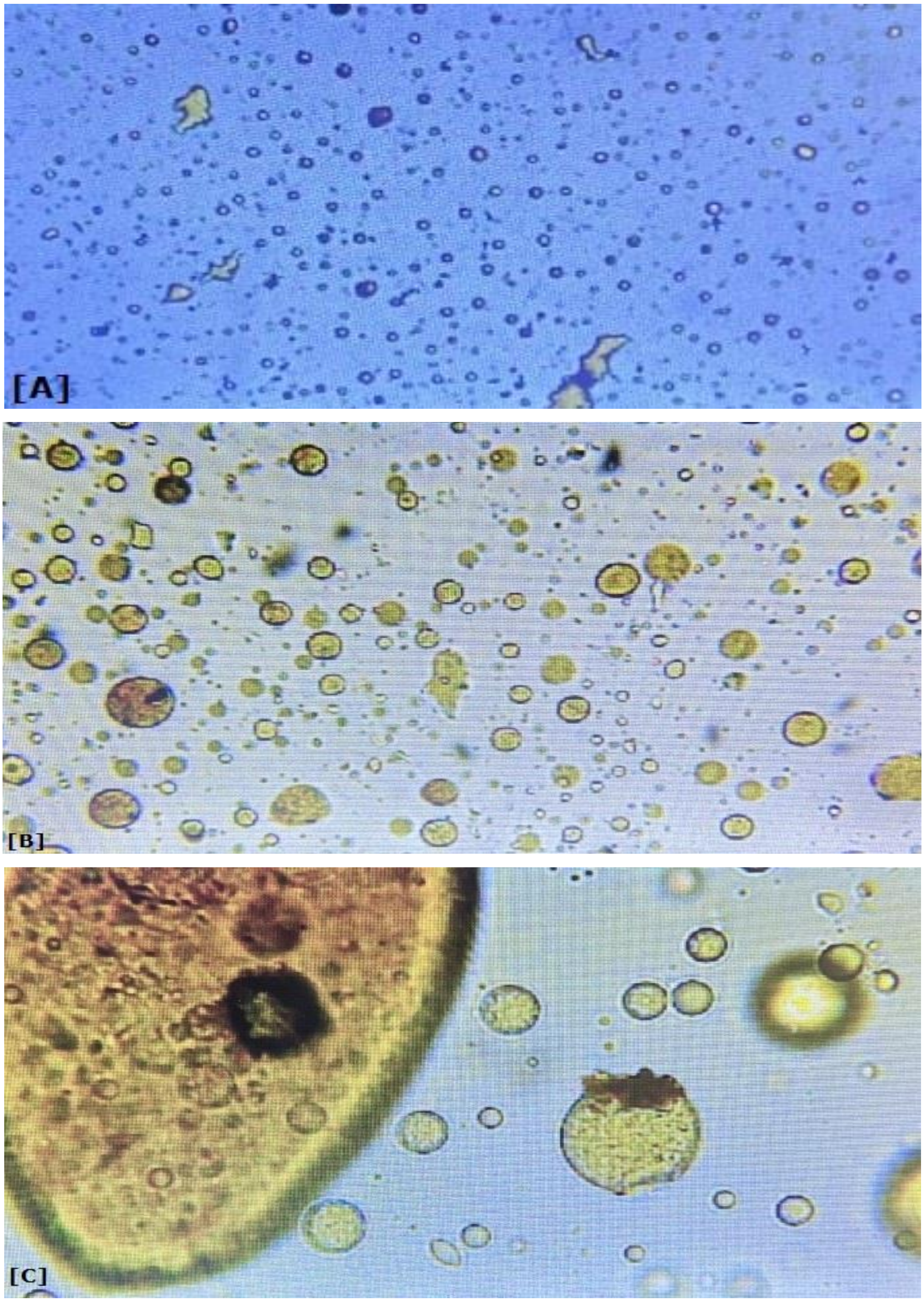


Figure 4.3 Microscopic image of 100% Biomass at different magnification levels: A=4X, B=10X, and C=40X

The feed image shows the presence of a large amount of water, as well as oil and some char particles of very small particle size.

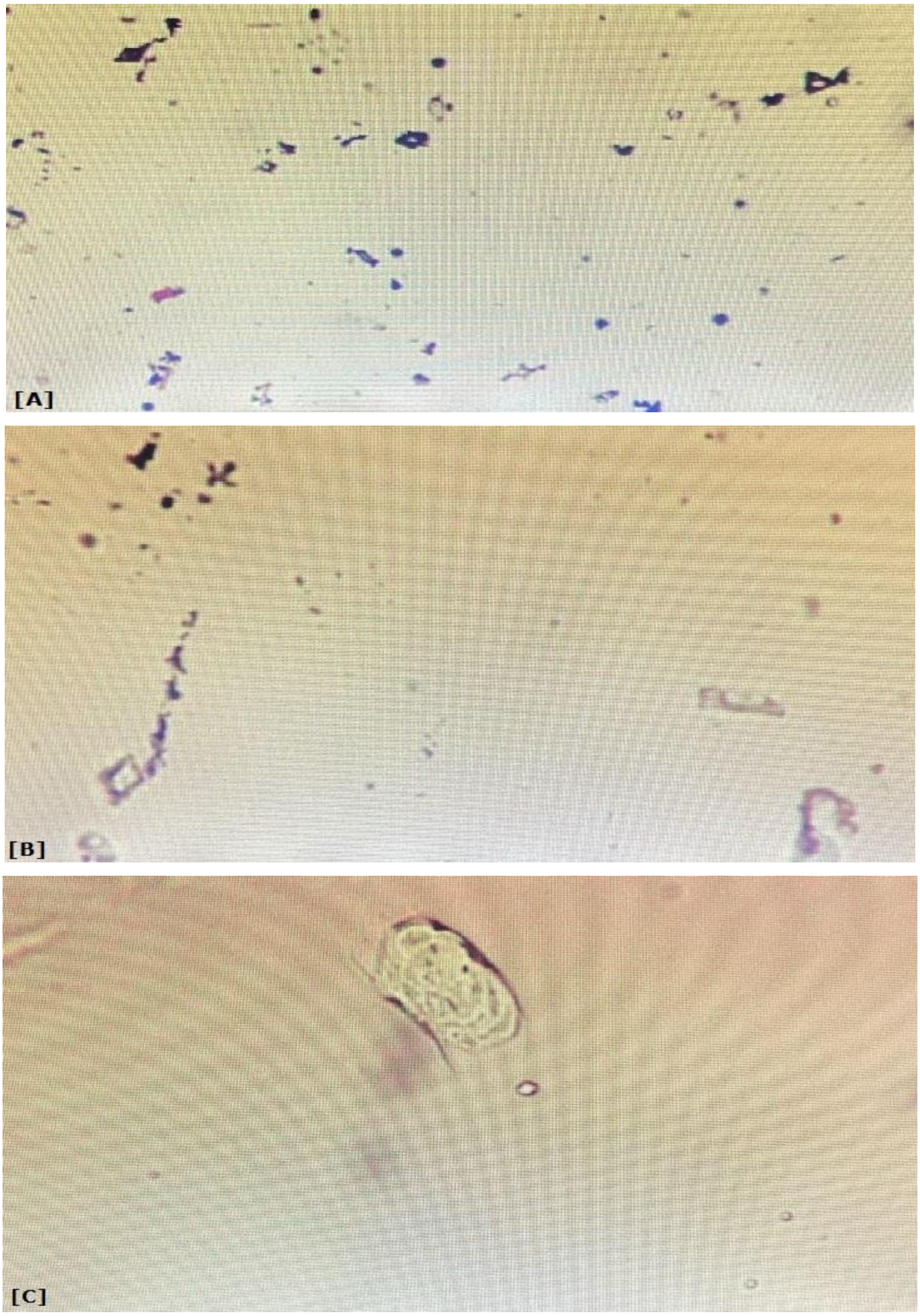


Figure 4.4 Microscopic image of 100% Oil shale at different magnification levels: A=4X, B=10X, and C=40X

The feed image shows the presence of a large amount of oil as well as some high molecular oil particles. Tar particles are visible in the images.

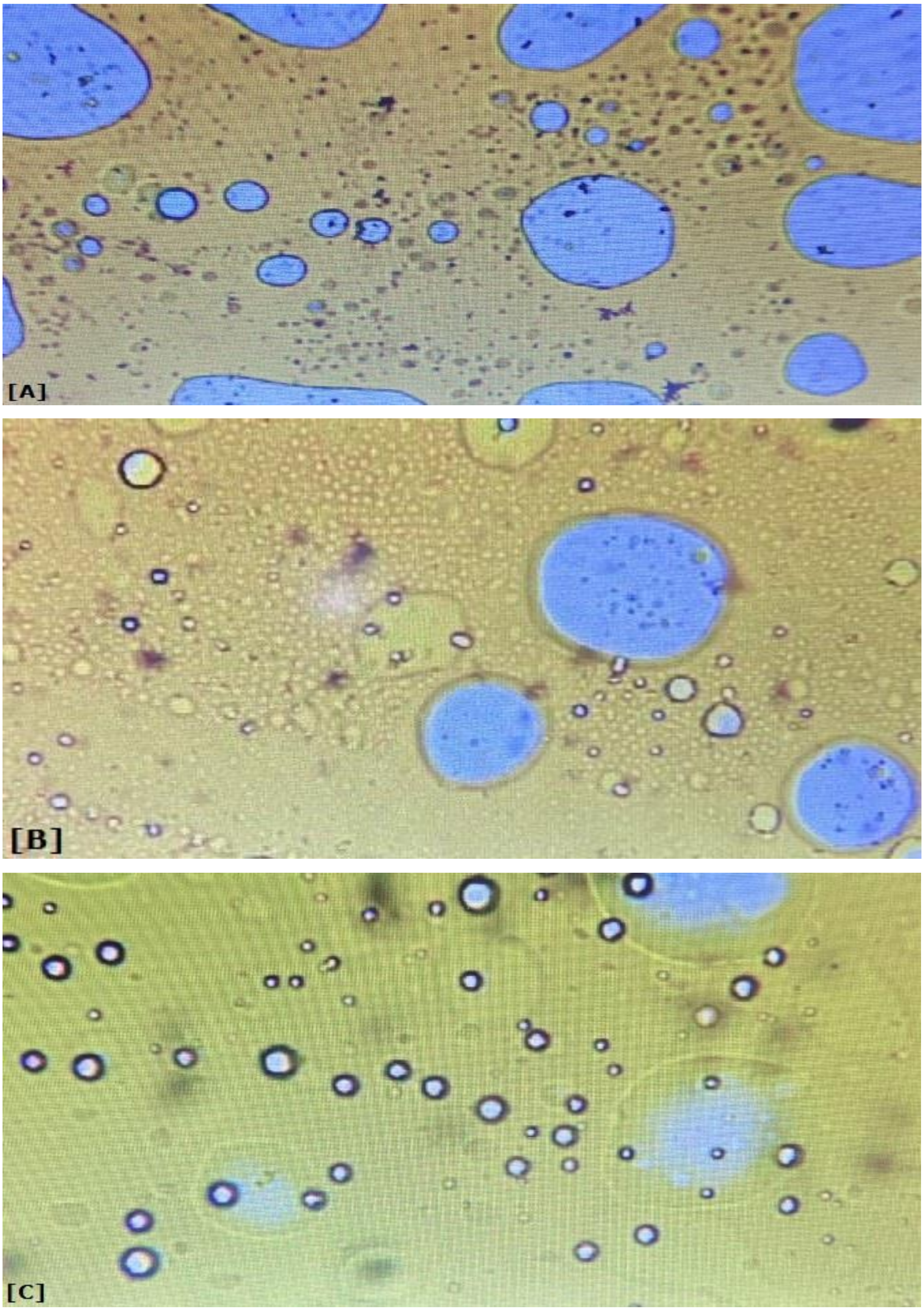


Figure 4.5 Microscopic image of 50% Oil shale and 50% Biomass at different magnification levels: A=4X, B=10X, and C=40X

The feed image shows the presence of water in almost equal proportion to that of the oil. The oil sample is heterogeneous as other different particles can be visually seen in the images.

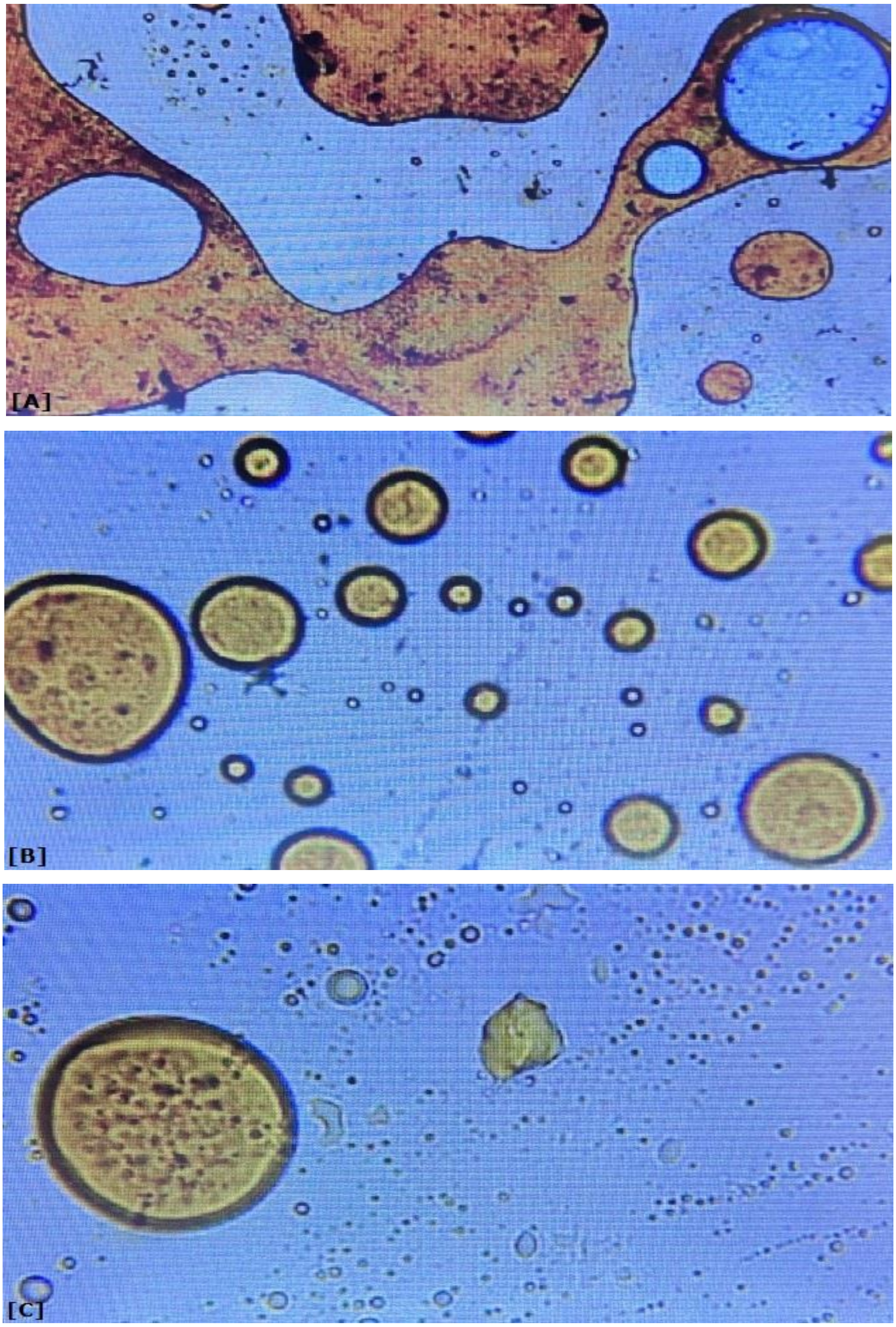


Figure 4.6 Microscopic image of 30% Oil shale and 70% Biomass at different magnification levels: A=4X, B=10X, and C=40X

The feed image shows the presence of a large amount of water as well as oil. The oil sample is heterogeneous as other different particles can be visually seen the image A.

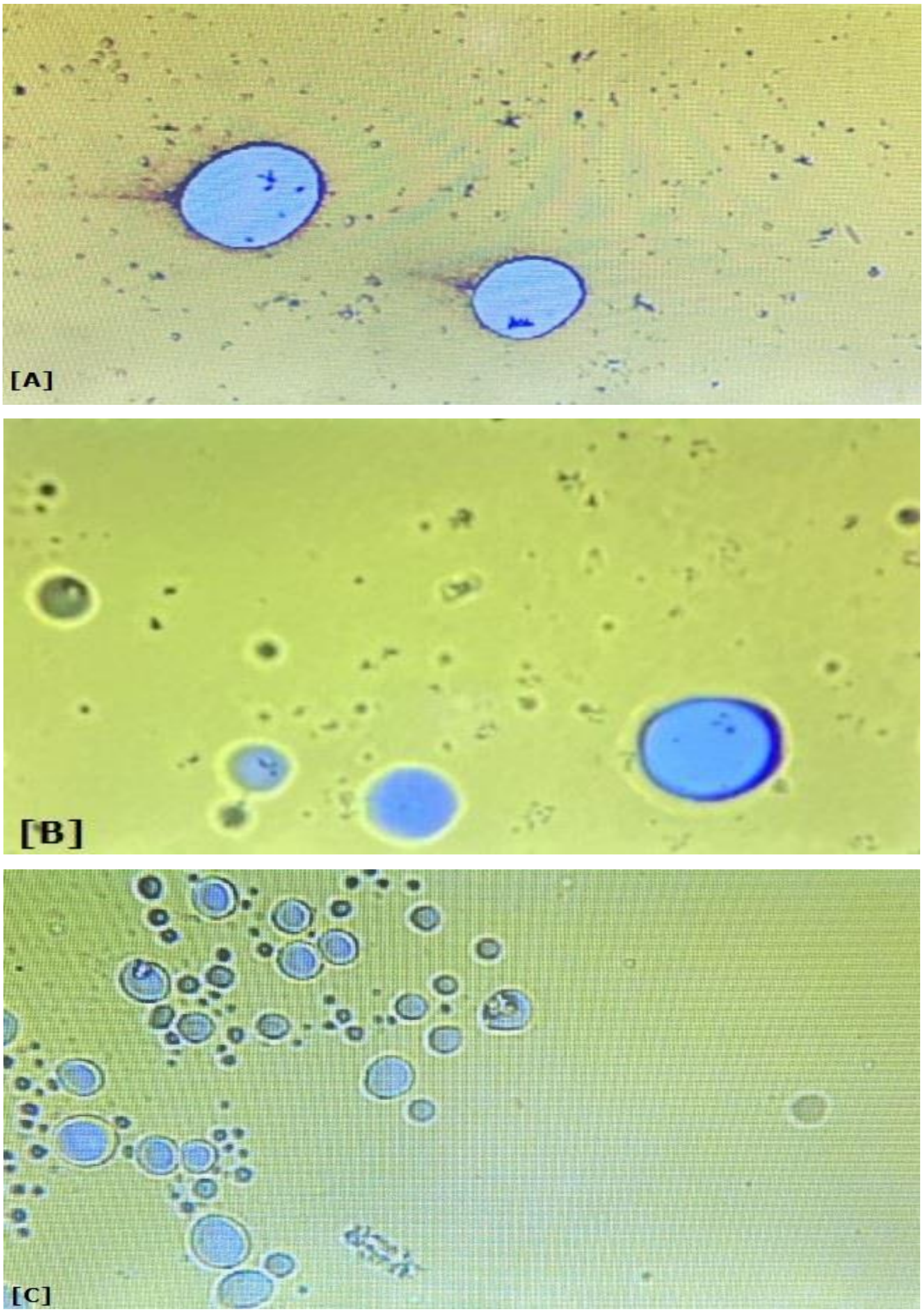


Figure 4.7 Microscopic image of 70% Oil shale and 30% Biomass at different magnification levels: A=4X, B=10X, and C=40X

The feed image shows the presence of a large amount of oil as well as water. Some tar particles are visible in the images.

From Figures 4.3-4.7, we can visually see the structure of the pyrolysis oil across the ratios. The structure of the pyrolysis liquid produced played a great role in the viscosity and density of the liquids. The 100% BM pyrolysis liquid (heterogeneous mixture) had the highest density value and the lowest viscosity value due to its water content, high oxygen content, and different organic compounds which could be seen visually in the feed images of Figure 4.3. This trend could be seen across the mixed ratio pyrolysis liquids where high BM content ratios produced more water content than oil, hence affect the density and viscosity values of the liquid producing a higher density value and a lower viscosity value when compared to mixed ratio pyrolysis liquid with high OS content. The 100% OS pyrolysis liquid (homogeneous mixture) had the lowest density value and the highest viscosity value due to its little to zero water content, and low organic content which could be seen visually in the feed images of Figure 4.4.

Char particles are hydrophobic [53], which makes them bind to the organic phase of the mixture, this can be seen in most of the images in Figure 4.3-4.7. The pyrolysis liquid produced by the mixed feedstocks was heterogeneous. Heterogeneity is expressed in two different phases - hydrophilic and hydrophobic (oily), the pyrolysis oils produced from the mixed ratios in the current study showed to some extent the hydrophilic phase as the oily phase of the mixture was suspended to some extent, this made the analysis of the oils quite difficult. The separation techniques of heterogeneous mixtures depend on the mixtures and the properties of the components ranging from distillation, filtration, and evaporation. The heterogeneous pyrolysis oil produced in the current study was not separated due to the low volume of oil produced as a result of the size of the feedstock the Fischer retort could handle at a time.

4.3.5 Gas chromatography-mass-flame Photometric Detector (GC-MS-FPD) analysis

Gas chromatography-mass spectrometry (GC-MS) is an analytical technique used to identify different volatile compounds in a sample. GC-MS combines the analytical tools of gas-chromatography and mass spectrometry to carry out the analysis. The GC-MS analysis for the current study was used to identify unknown peaks of the pyrolysis liquid. Gas chromatography-Flame photometric detector (GC-FPD) is an analytical technique use to detect sulfur and phosphorus compounds in a sample. The pyrolysis liquids produced by Fischer assay were diluted in acetone and then analyzed. The chromatogram in Figures 4.8-4.13 shows the different peaks that were recorded.

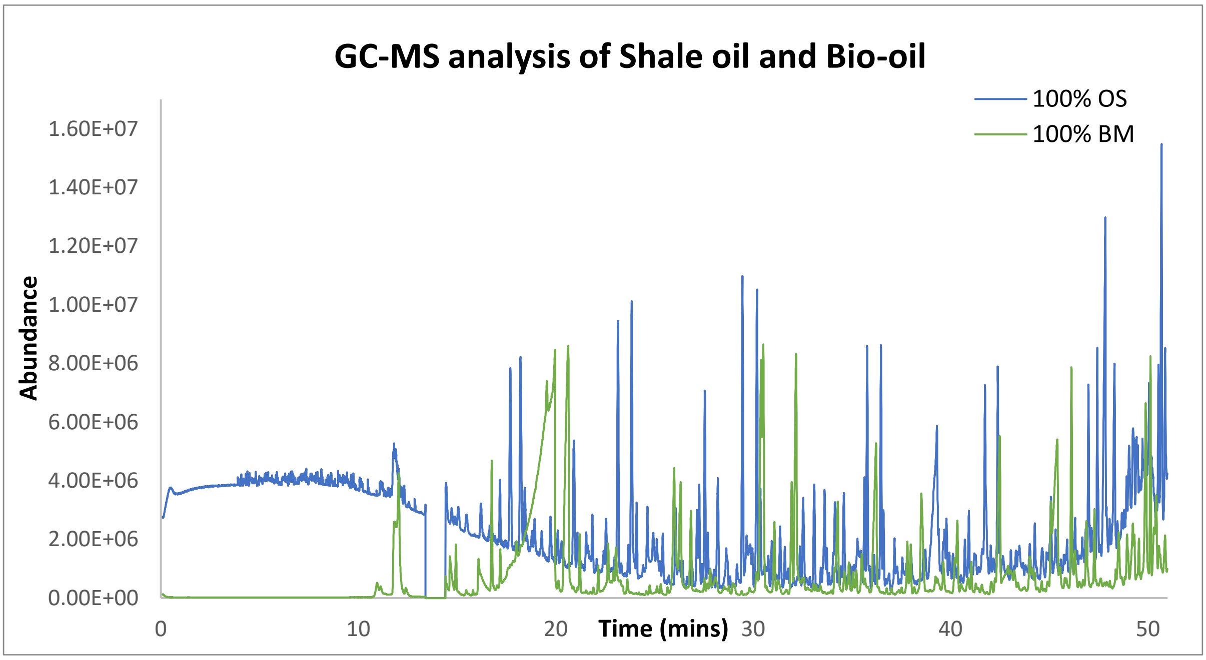


Figure 4.8 GC-MS analysis of Shale oil and Bio-oil

Figure 4.8 we could see some peak intensity of different compounds identified by the Gas chromatography-mass spectrometry. For 100% BM, some compounds identified by the analysis include acetic acid, phenol, catechol, different ketones, and furanes which are majorly hydrophilic compounds (have a high affinity for water). For 100% shale oil, some hydrocarbon compounds identified include hexene, hexane, octane, octene, decane, and other similar compounds. The shale oil contains mainly different alkanes, alkenes, and phenols which are majorly hydrophobic compounds (have low affinity for water). The compounds produced by the two different feedstock in the current study give us a good explanation as to why the pyrolysis liquid produced by the mixed ratio was a heterogeneous mixture.

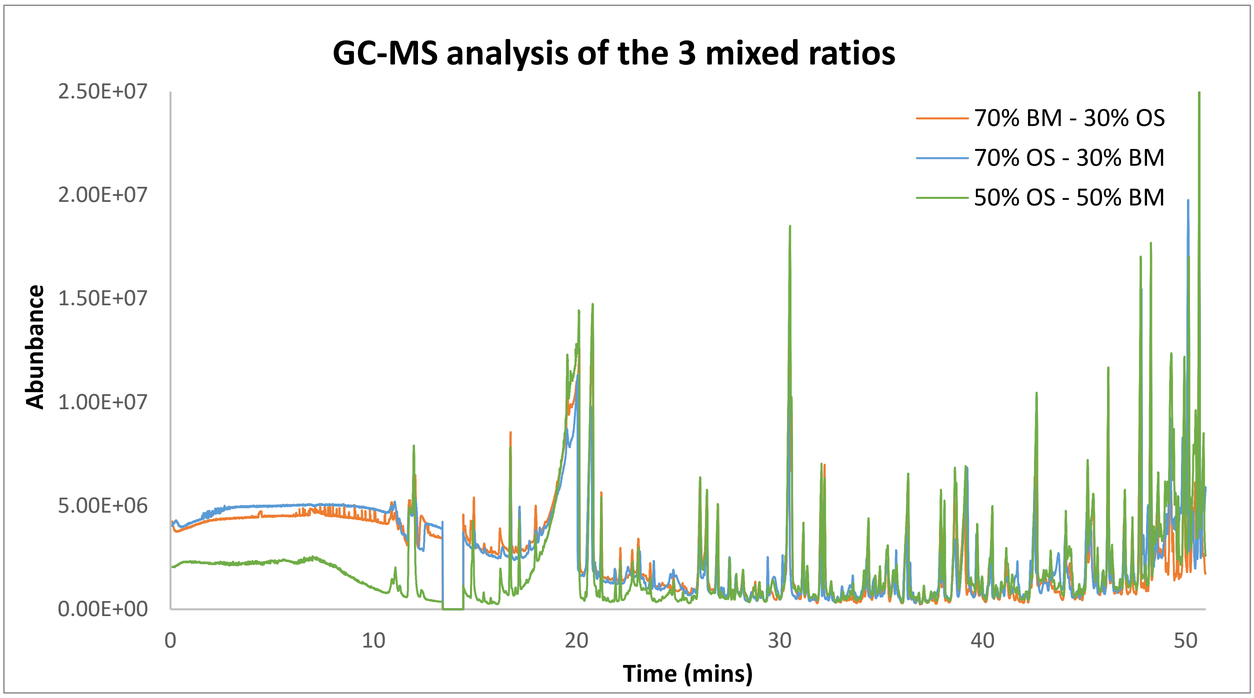


Figure 4.9 GC-MS analysis of the 3 mixed ratios

When compared to the rest of the oils produced, 100% OS contained the most sulfur content. 100% OS and 70% OS 30% BM oil contained most of the various sulfur compounds (about 13-15 compounds). The high content of hydrogen sulfide and sulfur dioxide in the 70% OS 30% BM mixture oil can be a result of the effect of oil shale as the majority of the feedstock is oil shale. But the presence of biomass was essential as water is necessary for good dissolution in getting the final product. Both 100% BM and 30% OS 70% BM oils contain 8-12 different sulfur compounds.

In general, 100% shale oil was characterized by a high content of various thiophenes, as well as heavier compounds, but also the absence of sulfur dioxide and methanethiol, while the oil shale and biomass mixed ratio oil was characterized by a large content of light sulfur compounds (H_2S, SO_2, CH_3SH).

Both 100% BM and the mixed ratio oils contained the following compounds: the three light sulfur compounds mentioned earlier in higher concentrations than other compounds, thiophene, 2-methyl thiophene, 3-methyl-1-butanethiol, 2-hexanethiol or 2-methyl-1 -pentanethiol, 2-ethyl-5-propyl-thiophene. The 70% OS 30% BM mixture oil contained alkylated derivatives of thiophene in addition to the aforementioned compounds.

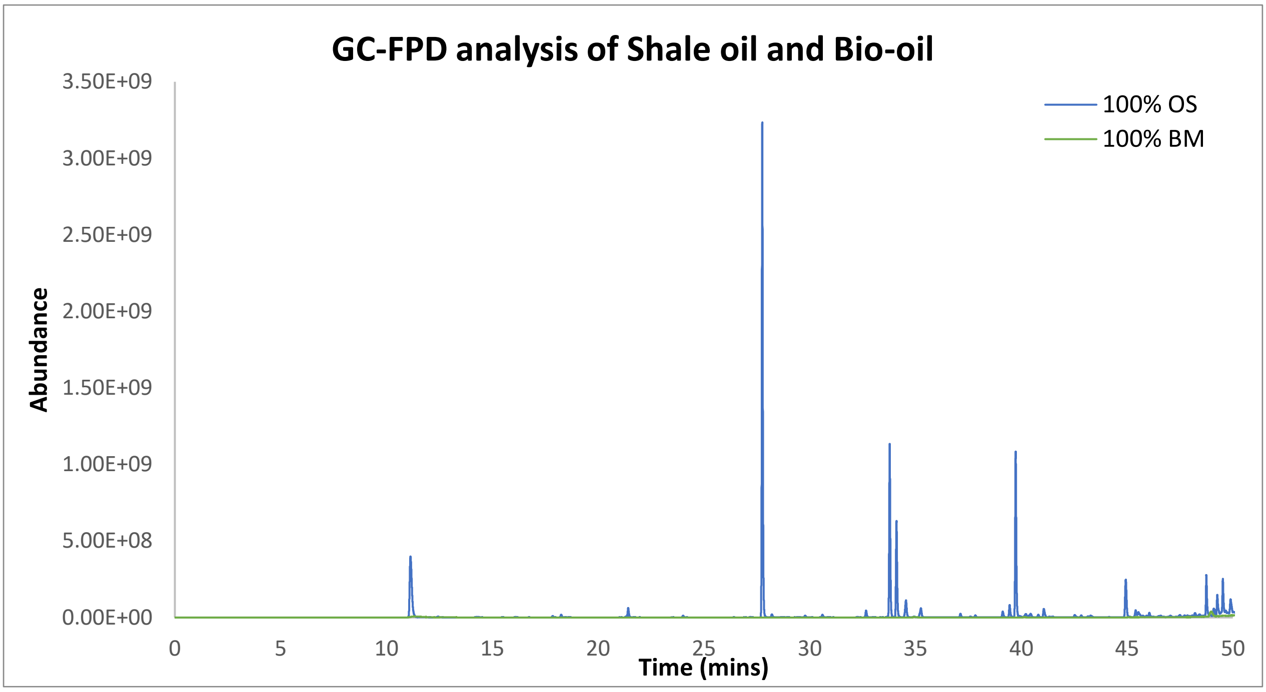


Figure 4.10 GC-FPD analysis of the Shale oil and Bio-oil

In 100% Bio-oil, a few more compounds were characterized than in the 50% OS 50% BM ratio oil, but these characterized compounds were at very low concentrations, only hydrogen sulfide (H_2S) gave a significant peak in the 100% bio-oil but this could not be seen in Figure 4.10 because of the low concentration when compared the that of shale oil. Figure 4.11 shows a zoomed-in GC-FPD analysis of the Shale oil and Bio-oil

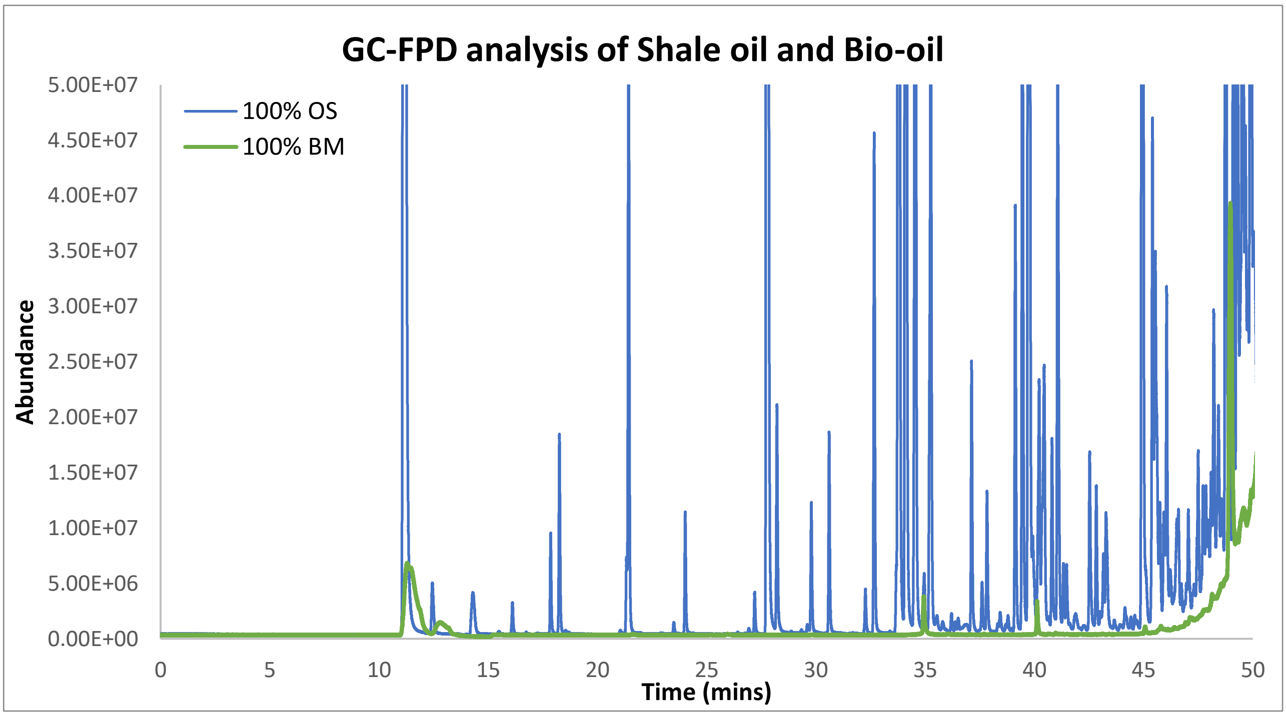


Figure 4.11 Zoomed-in GC-FPD analysis of the Shale oil and Bio-oil

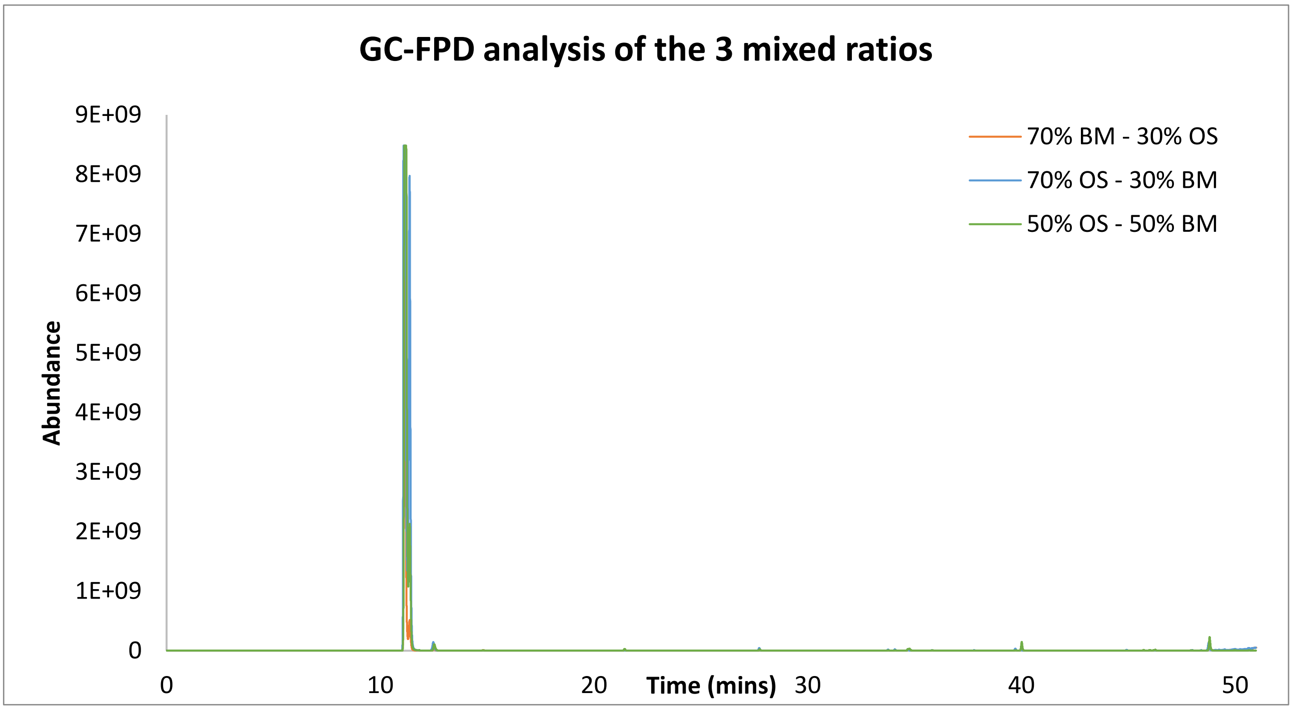


Figure 4.12 GC-FPD analysis of the 3 mixed ratios

The mixed ratio oils had similar peaks as seen in Figure 4.12, however, it is important to note that the 30% OS 70% BM oils also contained an unidentified compound at 35.8 retention time and was characterized by a higher content of 2-ethyl-5-propyl-thiophene than the 50% OS 50% BM ratio oil and 100% bio-oil.

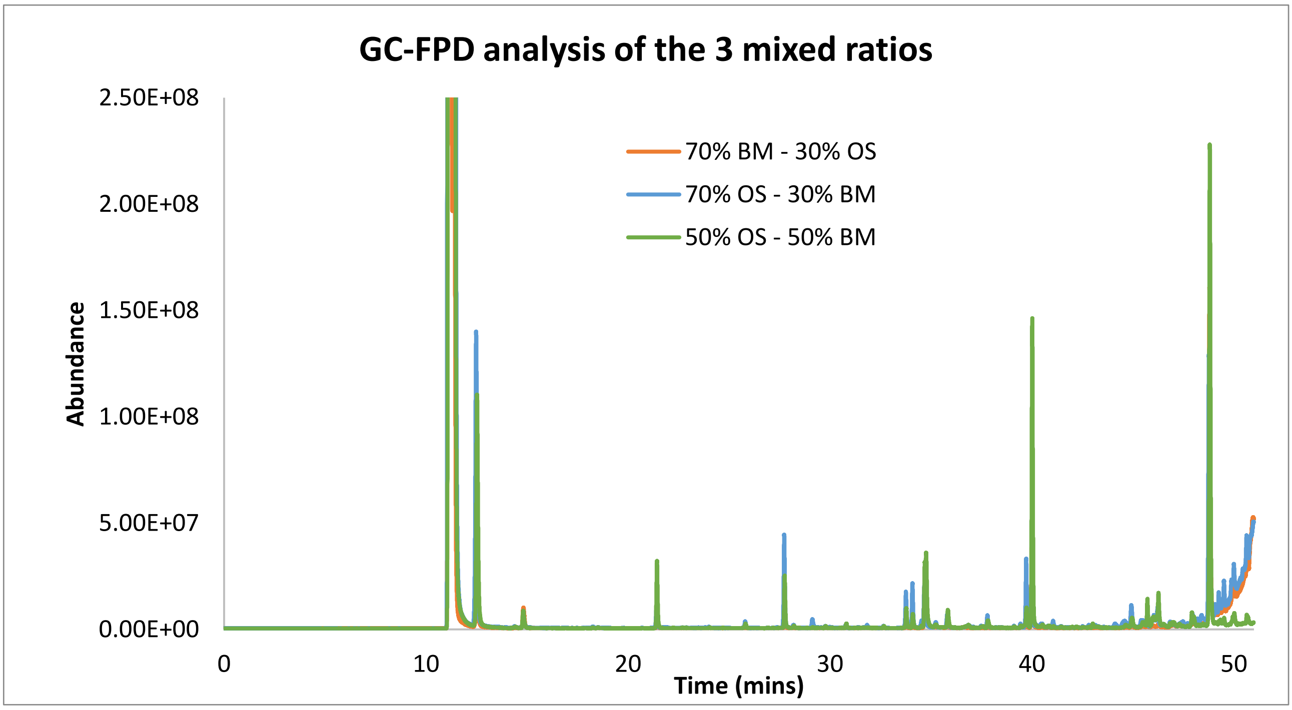


Figure 4.13 Zoomed-in GC-FPD analysis of the 3 mixed ratios

Table 4.16 Sulfur compounds of pyrolysis oil

Sulfur compound (divided 10^{10})	Retention time (mins)	Feedstock ratios				
		100% OS	100% BM	50% OS 50% BM	70% OS 30% BM	70% BM 30% OS
Hydrogen sulfide	11.2	9.04	0.260	65.36	64.16	54.49
Sulfur dioxide	11.3	-	0.030	16.83	15.92	4.81
Methanethiol	12.5	-	0.026	1.24	0.54	0.42
Unidentified	14.8	-	-	-	-	0.050
Thiophene (both NIST and compliant with our standard)	21.4	0.31	0.003	0.13	0.027	0.020
Unidentified	25.7	-	0.004	-	-	-
Thiophene, 2-methyl-	27.7	9.89	0.005	0.075	0.073	0.028
Thiophene, 3-methyl-	28.2	0.087	0.001	-	-	-
Thiophene, 2-ethyl-	33.7	3.88	-	-	0.030	-
Thiophene, 2,5-dimethyl-	34.1	2.28	-	-	0.033	-
Thiophene, ,4-dimethyl-	34.6	0.55	-	-	-	-
1-Butanethhiol, 3-methyl-	34.7	-	0.012	0.23	0.063	0.15
Thiophene, 2,3-dimethyl-	35.3	0.30	-	-	-	-
Unidentified	35.8	-	-	-	-	0.004
Thiophene, 2- (1-methylethyl) or 2-isopropyl	39.7	3.32	-	-	0.037	-
2-Hexanethhiol or 1-Pentanethhiol, 2-methyl-	40.0	-	0.006	0.42	0.037	0.15
Unidentified	44.0	-	-	-	0.042	-
Thiophene, 2,5-diethyl-?	44.9	0.92	0.002	-	-	-
Unidentified	45.7	-	-	-	-	0.009

Thiophene, 2-ethyl-5-propyl-	48.8	0.75	0.048	0.066	0.28	0.56
Unidentified	49.3	0.44	-	-	-	-
Thiophene, 2-(2,2-dimethylpropyl)-	49.5	0.73	-	-	-	-
Unidentified	49.9	0.50	0.004	-	-	-

Table 4.16 shows the different sulfur compounds found in the pyrolysis liquid at different retention times across all the ratios in the current study.

4.3.6 Heating value

The Heating value of a sample (solid or liquid) is the quantity of heat produced per kilogram/gram when burnt with the presence of oxygen in a bomb calorimeter. Table 4.17 shows the results of bomb calorimeter tests of the pyrolysis liquid produced by the Fischer assay method for the current study.

Table 4.17 Calorific value of pyrolysis oil

Feedstock Ratio	Heating value Feedstock (MJ/kg)	Heating value liquid (MJ/kg)
100% OS	9.01	22.06
100% BM	20.00	14.09
30% OS 70% BM	*17.00	17.01
50% OS 50% BM	*15.00	18.60
70% OS 30% BM	*12.00	20.20

(*) Estimated value

The table showed the average high heating value of raw oil shale to be about 9.01 MJ/kg and for the produced shale oil 22.06 MJ/kg and for Biomass, the average high heating value of raw black alder to be about 20.00 MJ/kg and for the produced bio-oil 14.09 MJ/kg. The heating value for the biomass was the lowest due to its high water content in biomass since the presence of water will influence the combustion process. The effect of oil shale can be seen across the 3 mixed ratios, the heating values increased with the increase in OS content in the mixed feedstock.

The heating value depends on the nature of the sample and the relative proportions of its elemental composition present. The heating value increases with increasing amounts of hydrogen and decreases with the moisture content present in the sample. In the current study, carbon (C), hydrogen (H), and oxygen (O) content played a major role in the calorific values of the liquid analyzed.

From the literature, we could that Shale oil produced by oil shale having a heating value range of 36-40 MJ/kg [12], however, the elemental composition of the oil shale had higher carbon (76.5%-77.5%) and hydrogen (9.0%-11.5%) content and lower oxygen content (9.0%–11.5%) when compared to the elemental composition of the oil shale used in the current study. Also, from the literature review, it was observed that the bio-oil produced from biomass had a heating value range of 13-26 MJ/kg [7], [19]–[23] making the result obtained valid.

5. Conclusion

The current study investigated the co-pyrolysis behavior of oil shale and biomass using Kukersite oil shale and Black alder as the key material. After careful literature research and analysis, Thermogravimetric analysis (TGA) and Fischer assay (FA) were the two methods used to study the co-pyrolysis behavior. The experiment carried out in the two methods was in an inert condition with the use of nitrogen gas (N_2) at different flow rates of 100 ml/min for TGA and 10 ml/min for Fischer assay. This was done in order to achieve pyrolysis at the desired temperature of 520 ^{o}C. The products of the pyrolysis process produced were char, pyrolysis liquid, and gas.

The mass loss result recorded across both methods for the different feedstock ratios was a result produced by the average of 2 runs of experiments for each feedstock ratio. The relative standard deviation result calculated from the average mean of the mass loss across the feedstock had a range of 1.38-5.92% in TGA, and 0.67-4.99% in the Fischer assay, which means the results produced were acceptable. From the mass loss result, 100% BM had the highest mass loss percentage due to its high organic content while 100% OS had the lowest due to its natural low water and organic content. This trend was evident across the mixed feedstock as ratios with higher BM content showed higher mass loss percentage when compared to those with low BM content and vice versa to mixed feedstock with more OS content. The result of mass loss across both methods was similar when compared and they followed the same trend of mass loss percentage according to the feedstock ratio.

Pyrolysis liquid (Oil+water) in the current study was obtained in Fischer assay experiments. The color of the liquid produced from the mixed ratios was dark brown having a smokey odor. From the result, we could see that 100% BM had the highest liquid yield percentage while 100% OS had the lowest. This trend was evident across the mixed feedstock as ratios with higher BM content showed higher liquid yield percentage when compared to those with low BM content and vice versa to mixed feedstock with more OS content.

The density of the shale oil produced in the current study was similar to past studies of kukersite oil shale. Bio-oils are complicated oils containing emulsified water and mostly oxygen containing organic compounds which affect the density of bio-oil causing it to have a higher value when compared to shale oil. This trend was evident across the mixed feedstock.

The effect of co-pyrolysis can also be seen in the viscosity values of the pyrolysis liquid. Shale oil produced in the current study was homogeneous with little or no pyrolysis water in it, thereby producing a higher viscosity value when compared to the liquid produced by the mixed ratio. Biomass had the lowest viscosity due to its chemical composition and high water content.

Gas chromatography-mass spectrometry-flame photometric detector (GC-MS-FPD) analysis was done on the pyrolysis liquid produced in the current study. Shale oil and 70% OS 30% BM contained about 13-15 different compounds. Bio-oil and 30% OS 70% BM liquid contained about 8-12 different compounds.

In the current study, the elemental composition of the feedstock such as carbon, hydrogen, and oxygen content played a major role in the heating values of the liquid analyzed. The heating value of the shale oil produced in the current study was lower than that recorded in the literature. This was a result of the difference in its elemental composition of the kukersite oil shale used for the current study. The heating value of the bio-oil in the current study was within the range of heating values reported in the literature. The effect of co-pyrolysis can also be seen in the heating values across the mixed ratio of the current study as ratios with higher OS content had higher heating values when compared to those with low OS content and vice versa to mixed feedstock with more BM content.

As a main conclusion, the method of co-pyrolysis of oil shale and biomass has good prospects for the integrated production of fuels taking into account the high yield of oil. Besides, this process could help reduce the sulfur content of fuel.

In the future, the study on the co-pyrolysis of oil shale and biomass should be done with a faster heating rate as the slow heating used in the current study would result in a heterogeneous mixture that cannot be fully used or analyzed.

5.1 JÄRELDUSED

Käesolevas uuringus uuriti põlevkivi (PK) ja biomassi (BM; must lepp). Protsessi uurimiseks kasutati kahte meetodit: termogravimeetriline analüüs (TGA) ja Fischeri analüüs (FA). Mõlema meetodi korral viidud katse läbi inertgaasi keskkonnas, kasutades lämmastiku (N_2) voolukiirustel vastavalt 100 ml/min ja 10 ml/min. Pürolüüsi lõpptemperatuuriks oli 520°C. Pürolüüsiprotsessi tulemusena saadi süsi, pürolüüsivedelik ja gaas.

Mõlema meetodi puhul korrati iga lähtematerjali seguga katseid vähemalt kaks korda. Katsetulemuste suhtelised standardhälbed, mis arvutati massikadude järgi, olid TGA puhul vahemikus 1,38-5,92% ja Fischeri analüüsi puhul vahemikus 0,67-4,99%. Suurim massikadu saavutati 100% BM-i korral tulenevalt tema kõrgest orgaanilise aine sisaldusest, samas kui 100% PK korral oli massikadu väikseim. Selline suundumus ilmnes läbivalt – mida suurem oli lähtematerjalis BM-i osakaal, seda suurem oli ka massikadu. Mõlemad kasutatud meetodiga saavutati pürolüüsil analoogsed massikao tulemused.

Pürolüüsivedelik tema omaduste uurimiseks saadi Fischeri analüüsil. Saadud vedelikud olid tumepruuni värvusega ja suitsuse lõhnaga. Sarnaselt massikaoga oli ka pürolüüsivedeliku saagis kõrgem 100% BM-i korral ning madalaim 100% PK korral.

Käesoleva töö käigus saadud põlevkiviõli tihedus oli samas suurusjärgus varasemalt mõõdetud väärtustega. Bio-õlid on keerulised valdavalt hapnikuühendeid sisaldavad segud, mis lisaks sisaldavad ka emulsioonina vett. Selle tulemusena on ka bio-õlide tihedus kõrgem kui põlevkiviõlil. Vastavalt BM-i osakaalule lähtematerjalis kasvas ka saadud pürolüüsivedeliku tihedus.

Koospürolüüsi mõju avaldub ka saadud pürolüüsivedelike viskoossuses. Põlevkivi pürolüüsil saadud õli oli homogeenne ning ei sisaldanud praktiliselt vett. Selle tulemusena ja tingituna tema keemilisest koostisest oli tema viskoossus kõrgem kui BM-i ja PK koospürolüüsil saadud pürolüüsivedelikel. BM-i pürolüüsil saadud pürolüüsivedeliku viskoossus oli madalaim.

Kõiki saadud pürolüüsivedelikke uuriti gaaskromatograafi-massdetektor-leek fotoionisatsioon detektor süsteemiga. Põlevkiviõli ja vahekorras 70% PK 30% BM pürolüüsil saadud pürolüüsivedelikud sisaldasid 13 kuni 15 erinevat väävliühendit. Lähtematerjalis põlevkivi sisalduse vähenedes väheneS ka väävliühendite arv pürolüüsivedelikes, olles 8 ja 12 ühendi vahel.

Töö tulemused näitavad, et lähtematerjali elementkoostisel on märkimisväärne mõju saadava pürolüüsivedeliku kütteväärtusele. Kuigi põlevkivi pürolüüsil saadud pürolüüsivedeliku kütteväärtus oli kirjanduse andmetest madalam, oli ta siiski märkimisväärselt kõrgem BM-i pürolüüsivedeliku kütteväärtusest. Viimase madal kütteväärtus tuleneb kõrgest veesisaldusest ja õli koostises olevast hapnikust. PK osakaalu kasvades lähtematerjalis kasvas ka saadava pürolüüsivedeliku kütteväärtus.

Töö peamise järeldusena võib välja tuua, et BM-i ja PK koospürolüüs on tulenevalt kõrgest õlisaagisest perspektiivne meetod vedelkütuste tootmiseks. Lisaks võimaldab see toota võrreldes põlevkiviõliga madalama väävlisisaldusega kütust. Küll aga tuleb tulevikus uurida koospürolüüsi suurematel kuumutuskiirustel, kuna madalate kuumutuskiiruste korral saadakse heterogeenne pürolüüsivedelik, mille analüüsimine ja kasutamine on keeruline.

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