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Fuel Range Properties of Oil and Wax Obtained from Linear Low Density Polyethylene Fluidised Bed Reactor (FBR) Catalytic Pyrolysis

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Abstract

Virgin linear low density polyethylene was subjected to pyrolysis in a fluidised bed reactor pilot-plant segmented into three heating zones with both sand and Magnofil BT 80 catalyst as bed materials. The pyrolysis oil and wax products were extracted at an average bed temperature of 600 and 700°C. The oil yield decreased between 600 (8.7 wt.%) to 700°C (8.1 wt.%) in a reverse effect with reaction time (358 and 384 minutes, respectively). This was attributed to the increase in the polyolefin polymer matrix's vibration, as a result of the absorbed thermal energy with the increase in temperature. The experiments at 700°C showed no wax formation but high yields of gaseous products and oils which are more lucrative in managing accumulated plastic waste, which polyethylene constituents' large proportions of via thermo-chemical conversion technologies. The estimated calorific value at 600°C was 45.5 MJ kg⁻¹ which is in the acceptable range for both diesel and gasoline fuel market specifications. The sulphur content in the pyrolysis oil was estimated as 0.013% and didn't get affected by change in temperature of the fluidised reactor. However, de-sulphurisation will be required in the future to have the oil within acceptable ranges of clean fuels. In addition, and to support this work's results in obtaining fuels from such feedstock materials; the fuel range hydrocarbons were also analysed. The diesel fuel hydrocarbon range (C₁₀-C₁₉) was between 37 to 60% in the pyrolysis oils examined. The results determined experimentally from the pilot-plant work herein are quite promising for sustainable fuel integration plans in the near future, namely with existing petroleum refining complexes.

Keywords: Polyethylene, FBR, Energy, Pyrolysis, Fuel.

1. Introduction

Plastic Solid Waste (PSW) accumulation has been causing the environment adverse effects and is still considered to be a major problem that requires quick intervention on a global scale. Within the United States (US) alone, some 5.715 million metric tonnes of high-density polyethylene (HDPE) waste were generated in 2018 as per the United States Environmental Protection Agency (EPA) assessment [1]. A mere 9% of this large PSW fraction of the total municipal solid waste (MSW) generated in the US, was collected for sorting and recycling and the remainder was landfilled (75%) and incinerated (16%). In more explicit terms, the US faces major PSW due to military bases and their reliance on plastic goods for meal wrappers, containers and other packaging elements which are generated at a rate of 0.3 kg per meal [2]. All of which are managed through pit burning which causes toxic emissions with harmful effects to both humans and the environment [3]. The facts about PSW are more drastic on a global scale and can present a more dire picture that requires immediate action too. As of the year 2021, there exist more 8.3 billion tonnes of plastic in the world with more than 6.3 billion classed as PSW [4]. Furthermore, the rate of PSW production is estimated as 300 million tonnes per annum as of late [5]. These figures are quite logical since the world has increased production capacity by 200-fold between the years 1950 (2 million tpa production capacity) and the year 2015 as depicted in [Figure S1 of the Supplementary Material File](#). It is also estimated that 30% of all plastics produced (2,500 million tonnes) are still in use to date, and that low (LDPE) and high-density polyethylene (HDPE) are the highest PSW types being produced annually at a rate of 57 and 40 million tonnes per annum, respectively [6]. [Table S1](#) presents important key statistics pertaining to the global situation of PSW.

The management of PSW is conducted via four main routes cumulatively referred to as the plastic waste management hierarchy [7-10]. It encompasses primary treatment methods which include in-house plastic scrap recycling within production lines and facilities. Secondary treatment methods include physical and mechanical recycling to produce acceptable market standards quality products overcoming the complexities faced due to the different types of polymer in the waste stream, additives and composites [11-12]. Tertiary methods include chemical treatments which encompass a wide range of technologies that alter the chemical structure of the plastic material stretching from thermo-chemical conversion (TCC) to biodegradation [13]. Finally, quaternary methods imply energy recovery via incineration.

In a more specific context within the Arabian Gulf Council Countries (GCC), the United Arab of Emirates (UAE) (37%, 4.4 million tpa) and the State of Kuwait (18%) rank as the highest generators [14]. Moreover, the State of Kuwait also possess according to World Bank Statistics, one of the highest daily per capita generation rates of MSW in the world estimated at 1.55 kg per capita per day [15-18]. This is attributed to a number of reasons mainly summarised as increase in population over a short span of time (last four decades), high rate of urbanisation, large proportions of food waste on consumer level and inflated gross domestic product (GDP) [19]. It is paramount to have an overview *Birdseye* view of

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3 the MSW situation to understand PSW rates and their accumulation manner in the region. Within the
4 GCC, the flow of plastics is notably high and has been estimated as 1.6 Mt \pm 82 Kt on an annual basis
5 which is equivalent to 13.7% of total MSW for the region [20]. Kuwait alone generates PSW estimated
6 as 18.2% of the total GCC load in the amount exceeding 220 K tpa [21]. The elevated generation rates
7 within the GCC and more specially Kuwait, has its deep roots in the economic growth and industrial
8 investments. Asian markets have intensified their ethylene production via investments in Kuwait, Saudi
9 and the UAE as of late [22]. The most common polymer types in PSW within the GCC are
10 polypropylene (PP), HDPE, LLDPE and LDPE [14]. However, more specially in Kuwait and based on
11 plastic film waste assessment, the most common polymer types are as follows [21]: LLDPE (46%),
12 LDPE (51%), HDPE (1%) and PP (2%). Almost all of PSW in Kuwait end up in open dumpsite where
13 unsanitary landfilling occurs [18] with no infrastructure to support waste management activities.

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21 The potential of conversion from tertiary chemical recycling of polyolefin (PO) PSW to high-end value-
22 added products, fuels and raw feedstock petrochemicals makes it a lucrative option to manage such
23 types of waste components. More specifically, pyrolysis of PO as a route of TCC can achieve high-end
24 value products, as well as advocate the recent circular economy (CE) and end of life (EOL) plastic
25 regulations published by the European Commission (EC) and adopted in many regions around the world
26 [23-28]. Pyrolysis is defined as a cracking technology in inert atmospheres that transforms plastics into
27 useful products relying on the degradation of the polymeric matrix subjected to controlled temperatures
28 and pressures [29-32]. When pyrolysed in the range between 400 to 700°C, PE has shown great potential
29 to produce straight chain paraffins and olefins products containing C₁-C₃₀. This is also dependant on
30 type of pyrolysis technique (e.g., thermal or catalytic), catalyst type, operating conditions and reactor
31 type as past works and reviews have shown [17,33-37]. These works have also pointed towards the fact
32 that the majority of pyrolysis works were conducted on batch, semi-batch or continuous reactors which
33 included mainly fluidised bed reactors (FBRs), which were found to be the most suited for catalytic
34 operation due to the possibility of catalyst reuse [38]. The only downside for FBR operation is the
35 handling of molten state sticky feedstock with the possibility of de-fluidisation when the feed sticks to
36 the reactor bed or when feed compartments are open for venting, pressure regulation or actual feeding
37 in continuous operation [8]. See aforementioned reviews for FBR past works and Table S2 for a
38 summary of main technical findings in literature pertaining to FBR pyrolysis. Another advantage of
39 FBR operation is the fact that it can achieve high mixing of catalysts to provide a large surface area for
40 the reaction [39]. On the other hand, pyrolysis of PSW can provide a viable fuel production route from
41 different feedstock to provide gasoline, diesel and wax products. This can not only achieve a CE but
42 can also support the increasing fossil fuel demand that leads to air quality deterioration associated with
43 NO_x, Sox and fine dust [40]. Furthermore, the global economy is now endangered by fossil fuel
44 resources depletion [41]. Fluctuating Prices are also a major concern that has affected the energy market
45 to a great extent which fuel from waste can help in stabilising them [34].

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3 In this work, the pyrolysis of the most common polymer type in PSW (e.g., PE) and more specifically
4 LLDPE, is achieved in a novel FBR system that was recently patented through the US Patent and
5 Trademark Office [42]. The oil and wax products under two different temperatures (600 and 700°C)
6 were tested after achieving full stability in fluidisation within the aforementioned FBR system. The aim
7 of this work was to study the fuel range properties of the products evolved using a catalytic operation
8 in pyrolysis mode that could simulate a route for PSW management. The work depicted herein can
9 easily be used as a platform for future plant commissioning in the GCC area for such operations to rid
10 the urban environment of SW accumulation with a potentially lucrative business on a pilot-plant scale.
11 To best of knowledge, the work on LLDPE FBR pyrolysis was not attempted in the past and the results
12 herein report it for the first time in literature using a novel set-up depicted from our research group for
13 this particular feedstock abundant in PSW [42].
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22 2. Materials and Methods

23 2.1. Feedstock

24 Virgin LLDPE was acquired through a local agent (Al-Issa Co. - State of Kuwait). The material was of
25 film extrusion grade used in the form of white translucent pellets (3 mm, $T_m = 124^\circ\text{C}$, melt flow index
26 (MFI) = 2 g/10 min, and $\rho = 0.918 \text{ g cm}^{-3}$ [34]. The thermal properties and degressive kinetics are
27 reported elsewhere [43]. Table S3 depicts the main properties estimated for the LLDPE feedstock
28 considered in this work. The degree of crystallinity determined for the LLDPE was 45%, falling in the
29 range of previous reports on semi-crystalline polyolefin polymers [44-46]. The moisture content
30 determined for the virgin plastics was between 0.03 to 0.06% which is almost equal to null (Table S3).
31 This is typically the case when commercial plastics are investigated [37,47-50]. The volatiles estimated
32 for the LDPE exceed 99% which indicates that the material favours the production of pyro-oils unlike
33 char/ash residues which promotes gaseous products (pyro-gas) evolution through cracking [47]. The
34 experimental thermograms obtained are presented elsewhere [34]. This is also in combination with the
35 ultimate analysis reported in this work for LLDPE showing carbon content of some 82% (Table S3),
36 the yield of high hydrocarbon products is promoted and expected. The results of the CV presented
37 herein are also in-line with previously reported research [48]. The CV estimated herein (45.48 kJ g^{-1})
38 favours the production of energy from LLDPE as a primary fuel source [42, 51].
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50 2.2. Reactor Bed Materials and Experimental Procedure

51 Two sets of experiments (in duplicates) were performed in the FBR system at an operating temperature
52 of 600 and 700°C. Both sets of experiments were conducted with sand as the fluidising bed material
53 and with the inclusion of olivine (Magnofil BT 80) as a bed additive catalyst [51]. The sand was
54 acquired through a local agent from Societe Nouvelle du Littoral Co. as a certified hydraulic 20-30 sand
55 - ASTM C778 (Silica = 99%, Bulk $\rho = 1590 \text{ kg m}^{-3}$ determined by EN933-1). The experiments were
56 performed using a mixture of sand (90 vol.%) and olivine (10 vol.%) as the bed materials [42, 51]. For
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3 this case, the weight of sand and olivine used were 1717 g and 168 g, respectively. The olivine catalyst
4 used was from ISO MAG Huttenbedraf Co. (Germany) with a declared bulk density of 1400 kg m^{-3} and
5 a chemical composition as per the following (wt.%): MgO (46.0 - 48.0), SiO₂ (39.0 - 41.0) and Fe₂O₃
6 (9.0). Pyrolysis experiments were conducted with the FBR system patented and described in detail prior
7 in Al-Salem et al. [42]. A nitrogen (N₂) flow of 10 L min^{-1} was used throughout the experimental runs
8 with a total of 5 kg of sample fed continuously in each run. The flow rate is equivalent to $1.4 U_{mf}^{-1}$
9 where U_{mf} is the calculated minimum fluidisation velocity [51]. Mixing performance and pressure drop
10 tests of the system can be found elsewhere [51]. The pyrolysis experiments were performed by keeping
11 the bed temperature at an average of 600 and 700°C and the cyclone temperatures were maintained at
12 300°C. Pyro-wax was obtained from the experiments of the 600°C and was collected in the collection
13 vessels below the cyclones and condensers. To supply the feedstock to the FBR, the screw conical
14 hopper, bucket conveyor, and rotary valve were operated at 40, 1000, and 800 rpm, respectively. Figure
15 1 below shows the system used in this work.

2.3. Elemental Analysis and Calorific Value

26 The main elements present (Carbon, Hydrogen, Nitrogen, oxygen and Sulphur) in the pyro-oil and wax
27 samples were measured using a LECO CHN828 and SC832 analysers by rapid combustion, where both
28 instruments were equipped with a thermal conductivity detector and flue gases pass through a
29 chromatographic separation column in accordance with the internationally recognised protocols of
30 ASTM D 5291-16 and ASTM D 1552-16, where the prior is used for CHN testing and the prior for S,
31 respectively. Samples in the approximate amount of $0.08 \pm 0.005 \text{ g}$ were used for the CHN analysis in
32 triplicate measurements with the approximate amount of 100 mg of Alumina Oxide (Al₂O₃) used in
33 each Tin capsule prepared for loading in the machine. Results were estimated against the Certified
34 Reference Material (CRF) of LECO Paraffin Oil (St. Joseph, Michigan/USA) No. 502-901 (C:
35 $86.4 \pm 0.5\%$, H: $14 \pm 0.1\%$, HV: $19831 \pm 27 \text{ BTU/lb}$) as a chemical standard. LECO Calibration sample lot
36 No. 1037 (Hydrocarbon) was used as a CRF for sulphur analysis (S: $1.99 \pm 0.02\%$) using a sample weight
37 of approximately $0.1 \pm 0.001 \text{ g}$ in duplicate measurements. Figure S2 shows the CHN analyser used in
38 this work and Figure S3 depicts operating conditions of the instrument thereafter. Figure S4 shows the
39 Sulphur analyser used and Figure S5 depicts a summary of the analytical method used for Sulphur
40 detection. A LECO AC 600 calorimeter was used to determine the gross calorific value of the pyrolysis
41 products. The samples of the amount $0.4 \pm 0.0001 \text{ g}$ was weighed and loaded into the crucible chamber
42 and tied with the cotton wire. Deionized water was added to the cartridge through the water circulation
43 system to fill the instrument's jacket and bucket, and the crucible holder was automatically placed into
44 the oxygen cartridge. Subsequently, the calorific value of the samples was determined and the test
45 procedure followed ASTM D 4809-18. Results were estimated against the Certified Reference Material
46 (CRF) of LECO Paraffin Oil (St. Joseph, Michigan/USA) lot No. 1001 (C: $86 \pm 0.5\%$, H: $14 \pm 0.1\%$, HV:

19831±27 BTU/lb) as a chemical standard. Figures S6 and S7 show the calorimeter used and the method parameters.

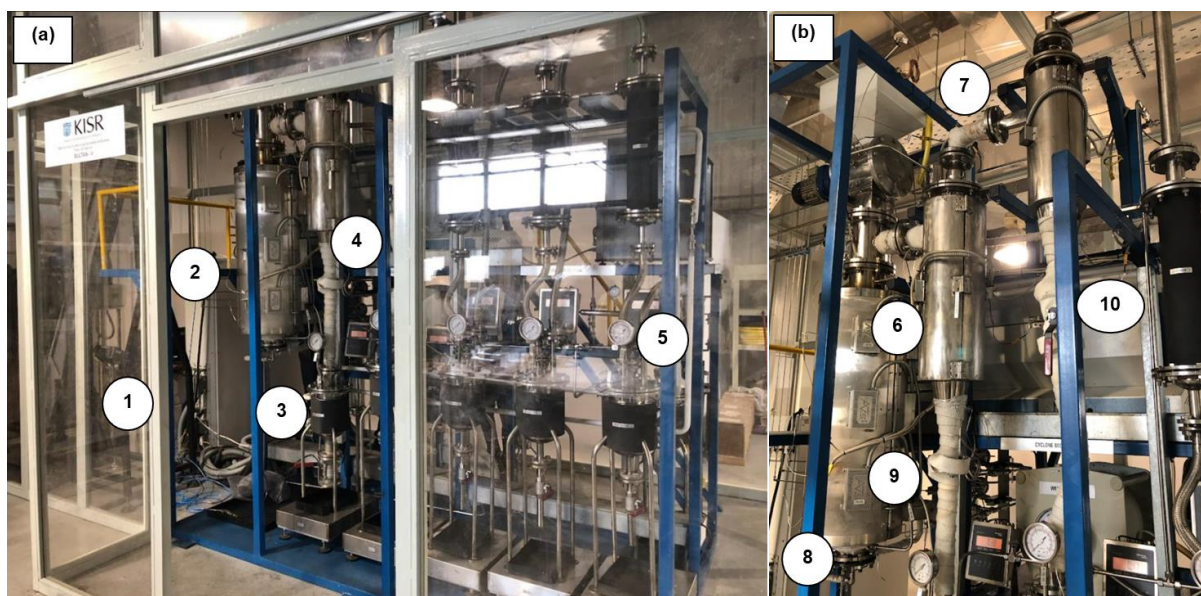


Figure 1. Pilot plant picture used in this work showing in figure (a): 1. Controllers and SCADA, (2) Conveyer belt reaching to feeding hopper and arrangement, (3) FBR - Casing furnace and bed, (4) Cyclones and (5) Gas trap; and in figure (b): (6) Cyclone #1, (7) Cyclone #2, (8) Gas feed, (9) Weighing balance, and (10) Condenser. Image source Salahudeen et al. [51] reprinted with permission.

2.4. Gas Chromatography-Mass Spectrometry (GC/MS) Characterisation

The identification of chemicals of fuel range such as naphtha, petrol (gasoline) and diesel were conducted using an Agilent 8890 Gas Chromatograph (GC) System. Solid phase extraction was conducted on each specimen of oil intended for testing whereby Thermo Scientific TM HyperSepTM Silica Cartridges with 40 to 60 μm particle size, 1 g bed weight; 6 ml column volume have been used. Analytes were eluted by a 6.0 ml Dichloromethane with a polarity similar to target compounds before GC injection. A thermal conductivity detector (TCD) and A flame ionisation detector (FID) were used to examine HCs components in the injected samples. The analysis was conducted for each chemical compound detected by the online Agilent Technologies library report, as well as, the lumped products analysis for $\text{C}_6\text{-C}_9$ (petrol/gasoline), $\text{C}_{10}\text{-C}_{19}$ (Diesel) and C_{19+} (wax). The configuration used is detailed in Table 1 and the detailed acquisition method is detailed in Figure S8 for the reader's consideration.

Table 1. Gas Chromatograph (GC) System Conditions and Configuration. Method Source Adapted from Al-Salem et al. [7].

Condition/Parameter	Value
Equipment	Agilent 8890 Gas Chromatograph (GC) System (Agilent Tech.)
Column(S)	FID: Agilent 19091Z-530, HP-1 TCD: Agilent 1.7 m Hysep+1.5 mo and Agilent 2ft Hysep A
Carrier Gas	Helium
Injection Temperature	250°C
Total run time/equilibration time	74 min/0.1 min (oven)
He Split Ratio	80:1
Oven Temperature	35°C (hold 1 min)/5°C min ⁻¹ heating rate
Sample wash volume/draw speed	8 µl/300 µl min ⁻¹

3. Results and Discussion

3.1. Yields and Mass Balance

The mass balance of the experimental runs based on the averaged lumped products of the pyrolysis process (*i.e.*, gas, oil, char and wax) is presented in Figure 2 which was calculated based upon the formulation below [52] and the individual product yield as per the one thereafter [34-35]:

$$\text{Pyrolysis (total gas) yield (\%)} = 100 - [\text{Total Oil (\%)} + \text{Total Wax (\%)} + \text{Total Char (\%)}] \quad (1)$$

$$\text{Pyrolysis (p) yield (\%)} = \frac{m_p}{m_f} \times 100 \quad (2)$$

where m_p is the mass of the weighted pyrolysis product fraction (g) and m_f is the total feedstock mass (g). The products discussed herein represent the total evolved yields in the whole FBR system indicating a total evolution of 100% of the feedstock (*i.e.*, full conversion). The increase in operating temperature led to a proportional increase in the total gas yield reaching a total of 91.4% (688 g) at 700°C (Figure 2). In contrast, the oil yield decreased slightly between 600 to 700°C from 8.7% (438 g) to 8.1% (405 g) in a notable proportional effect. No waxes evolved at the elevated temperature of 700°C which was expected for two reasons related to the fact of the matter which is the decrease in degradation activity of the LLDPE feedstock [53]. Higher temperatures, typically above 550°C, will result in the accelerated reach of polyolefin polymers to molten state prior to degradation. This will also increase their degressive products evolution (*e.g.*, non-condensable gaseous components) due to primary reaction cracking which decreases and eventually eliminates wax formation. The second reason is pertaining the actual design of the FBR bed used in this work. The reactor's bed is heated via three zones to deliver a more uniform heating across the reactor profile which heats the bed material more uniformly and at a higher speed as well (total run time was 384 minutes for the 700°C experiment) [42]. This also gives the polymer less time to reach molten state which results in delivering waxes up to 600°C in contrast to prior works

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3 where it was eliminated at lower temperatures ($\approx 500^\circ\text{C}$) [54]. In the case at hand herein, 700°C showed
4 no wax formation but high yield of gaseous products and oils which are more lucrative in managing
5 accumulated PSW via TCC technologies as both gas and oils could be utilised as standalone products
6 or recycled within the FBR system.
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9 Typically, PE pyrolysis gas evolved from FBR units will contain large proportions of hydrogen (H_2),
10 methane (CH_4), ethene (C_2H_4), ethane (C_2H_6), propene (C_3H_6), butene (C_4H_8), and 1,3-butadiene [53].
11 The typical pyro-gas produced from various pyrolysis regimes and reactors will also possess a high CV
12 between 42 and 50 MJ kg^{-1} that makes it quite lucrative as a heating source for the actual pyrolysis
13 system (or as a standalone product) [8,55]. Furthermore, the fact that these gases contain raw
14 petrochemicals such as ethane (C_2H_6), propene (C_3H_6) and butene (C_4H_8) makes it quite a profitable
15 petroleum downstream product for monomer recovery especially in GCC countries that have high SW
16 accumulation problems at one end and vast investments in petrochemicals on the other [47]. Therefore,
17 the utilisation of such processes in the region from PSW which contain LLDPE as a prime component;
18 can open major opportunities in the near future if designed as an integrated petroleum industry. Pyro-
19 gas is a direct result of the homolytic dissociation and β -scission reaction that occur to the PE when
20 pyrolysed and exposed to heat past its melting point [34,53,57-59]. The proportional increase with
21 elevated temperatures in this work could be directly attributed to the increase in the polyolefin vibration
22 as a result of absorbed thermal energy in the branched LLDPE matrix. It is therefore deduced that
23 LLDPE in the FBR's bed occupies higher energy states with elevated temperatures and prolonged
24 residence times for pyrolysis reaction [53]. This also points that C-C bonds length of LLDPE have
25 increased resulting in a decrease strength of the bond as well. The decrease in the C-C bond's strength
26 will also result in yielding small molecules of the FBR unit such as olefins in the range of C_2 - C_4
27 considered to be of immense petrochemical feedstock value.
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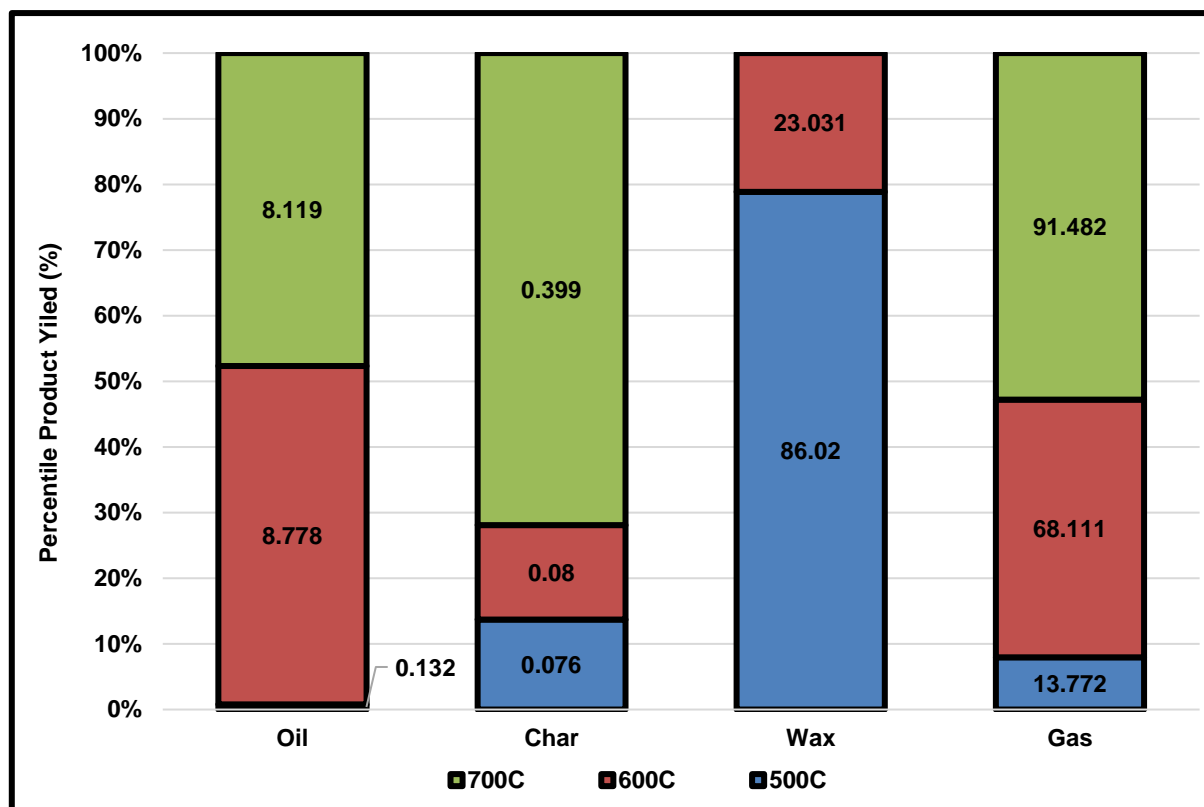


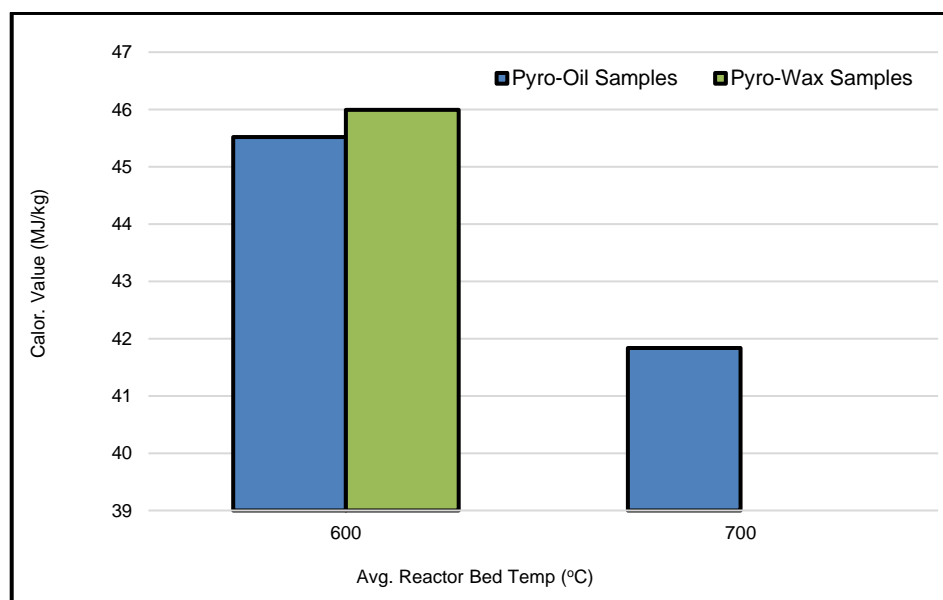
Figure 2. Product mass balance with respect to average reactor bed temperature ($^{\circ}\text{C}$). Products from 500°C were not analysed in this work as focus is on pyro-oils obtained but shown here for the reader's consideration in this section.

There exists a vast body of literature that shows PE pyrolysis gaseous yields in FBR units with various catalysts within the range from 6 and 93 wt.% in the operating temperature range between 500 to 797°C [60-63]. It is also established in literature that prolonged residence times with elevated temperatures increases the pyro-gas yield, as aforementioned herein and in-line with results compared from this work on LLDPE and other PE grades (HDPE, LDPE) [8-10,33,61]. The effect of catalysts used in FBR PE pyrolysis was also discussed prior by other authors. In this work, an amorphous acidic silica based (SiO_2 , 39.0 - 41.0 wt.%) was used in each experimental run's loading of the reactor bed. The Bronsted acid sites in such catalysts possess ionisable hydrogen atoms and Lewis's acid sites that favours production of gaseous products [33,64-66]. The oil yield decreased between 600 to 700°C in a reverse effect with reaction time (358 and 384 minutes, receptively). Past work on the same particular grade in thermal (non-catalytic) pyrolysis using a fixed bed showed that 600°C was the optimal oil yield temperature compared to LDPE [34]. This was attributed to the fact that PE favoured primary reaction cracking and to the contrary was in an inverse relationship with naphthalene and BTX yields in gaseous phase too. PE polymer is attracted on a molecular level by Van Der Waals forces which facilitate the vibration of molecules with heat that produces variety of non-condensable gases with elevated temperatures. This on the other hand, reduces pyrolysis oil evolution with temperature as well and

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3 results in pyrolysis waxes similar to the case at hand when 600°C is used. Past works on PE pyrolysis
4 indicated that pyrolysis oil maximum yields are produced at temperatures of 600°C or below in
5 agreement with the work at hand [33].
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8 3.2. Properties of pyrolysis oil and wax 9

10 **Figure 3** shows the calorific value estimated for both the pyrolysis oil samples obtained at 600 and
11 700°C; and the pyrolysis wax samples obtained at 700°C. The standard error (se) in all experimental
12 populations was less than 0.03 MJ kg⁻¹ with an average for pyrolysis oil estimated as 45.5 MJ kg⁻¹ at
13 600°C and 41.8 MJ kg⁻¹ at 700°C. A decreasing trend of calorific value was observed as a function of
14 reactor bed temperature (°C), which is attributed to the residence time increase resulting in less oil yield
15 of condensable hydrocarbons (HCs) [67]. The calorific value at 600°C is within range of diesel fuel
16 which ranges between 42.8 and 45.8 MJ kg⁻¹ and gasoline's range of 43.4-46.5 MJ kg⁻¹ [33].
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42 **Figure 3.** Pyrolysis Oil and Wax Calorific Value (MJ kg⁻¹) as a Function of Average Reactor Bed
43 Temperature (°C).
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47 The pyrolysis oil samples contain various organic HC species which are analysed and detected by GC-
48 MS as depicted in the next section for their fuel ranges. The lesser the residence time and the presence
49 of bed material in contact with the LLDPE favoured the production of oils. Longer residence times also
50 favoured the secondary cracking reactions in the FBR unit which eliminated wax production at 700°C.
51 Pyrolysis was from PE is produced as an intermediate product in the primary reaction pathway that gets
52 reduced at elevated temperatures [35]. The calorific value of the wax recovered in this work was
53 estimated as 45.9 MJ kg⁻¹ (**Figure 3**). The calorific value of waxes is directly dependent on the its
54 properties and the feedstock's, namely the chain length, C/H ratio, and aromatic content [68]. Past works
55 on pyrolysis wax puts its calorific value in the range of 44.5 and 45 MJ kg⁻¹ [69]. This shows that waxes
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recovered in this work have a great potential as a fuel source as well when compared to conventional fuels on the market.

Table 2 depicts the elemental analysis of the oil and wax samples obtained at different temperatures of pyrolysis in the FBR. The level of N detected in the oil and wax samples was near zero, which shows that majority of which was attached to molecules in the gas phase product. As for the main constituent of the samples, it was C and H. The C content remained almost identical with the change in temperature of reaction for the pyrolysis oil, but in the case of H it decreased from 12.3% (600°C) to 7.9% (700°C). The constant C content indicates that the carbonisation level was similar and didn't get affected by the change in temperature [8]. The results herein also indicate that majority of the N in the feedstock (**Table S3**, 0.13%) has been eliminated by the pyrolysis process leading to a concoction of HC based oil.

Table 2. Elemental Analysis of the Pyrolysis Oil and Wax Samples as a Function of Average Reactor Bed Temperature (°C).

Reactor Bed Temp. (°C)	C (%)	H (%)	N (%)	S (%)	O (%)
Pyro-Oil Samples					
600	83.55±0.66	12.32±0.05	0.03±0.01	0.013±0.005	4.09±0.001
700	84.40±0.36	7.96±0.84	0.02±0.15	0.013±0.00	7.60±0.005
Pyro-Wax Samples					
600	76.83±0.05	11.92±0.05	0.03±0.01	0.004±0.001	11.22±0.001

The S content in the pyrolysis oil samples was minimal and much lower than the levels in pyrolysis oil extracted from thermal pyrolysis of the same feedstock previously presented in Al-Salem et al. [34] which reached 2.44% at 800°C. The S content in this work was estimated as 0.013% and didn't get affected by change in temperature of the FBR process (**Table 2**). The feedstock material contained some 2.66% of S which is quite normal due to its presence in additives compounded with polymeric commodities [70]. This shows that the pyrolytic reaction has led to initialising a cracking reaction to remove the S content from the pyrolysis wax (as intermediate stage) and oils. This also indicates that sour compounds cleavage occurred with N-S and S-C bonds leading to their removal from the oil samples [71-74]. This also supports past claims that desulphurisation is required to reduce S content in both the oil and wax S to reach either 0.9% for light fuel oil or 0.1% (1000 ppm) for class D diesel specifications [34-35,75-77].

3.3. Chromatographic Analysis and Fuel-Range Identification

It is paramount to assess each sample extracted from this work to fossil fuel origins and conventional petroleum refining cuts. This is achieved herein based on the hydrocarbon ranges identified as lumped

products to determine the fuel potential in each analysed sample (e.g., pyro-oil and waxes) as per the following: C₆-C₉ (petrol), C₁₀-C₁₉ (diesel) and C₁₉₊ (waxes) [34,78].

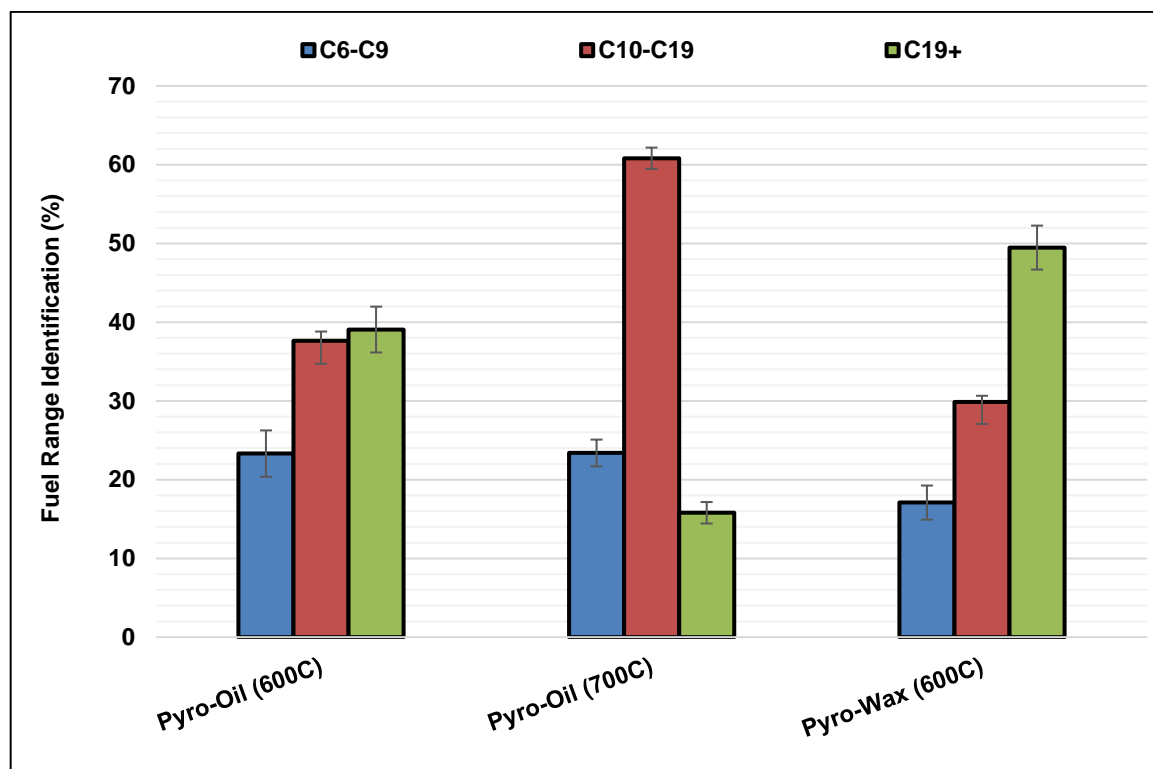


Figure 4. Fuel Potential Estimated for the Pyrolysis Oil and Wax Samples.

The oil samples studied in this work showed a large number of peaks that matched a variety of alkenes and aromatic hydrocarbons. The molecular weight increased with increasing retention times, as heavier molecules interact longer and elute later on in the column [34] (Table S4). The retention time of the oil samples up to about 20 minutes revealed typical alkenes expected in pyrolytic oil samples, in addition to aromatic hydrocarbons such as hexene, octane, decane, ethylbenzene and naphthalene. Figure 4 shows the fuel range hydrocarbons as a function of the reactor bed temperature for the pyrolysis oil samples. The diesel fuel range were most abundant which constituted 37% in the 600°C samples and 60% for the 700°C samples. The hydrocarbons detected were also in the range of past works on pyrolysis oils [79-80]. The increase in temperature to 700°C also favoured the production of polyaromatic hydrocarbons (PAH) which is also consistent with past works on FBRs as a result of aromatization and rearrangement reactions of aliphatic and monocyclic compounds expected with high temperatures [67]. Wax sample analysed has for apparent reasons favoured the wax range chemicals but also showed about 30% diesel range. It is therefore best recommended that oil samples are to be refined further for potential petroleum integration plans as a pathway for circular economy. This way, plastic waste (and solid waste

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2
3 in general) is utilised a sustainable feedstock for future integration plans that can produce fuels to reduce
4 reliance on typically fossil ones.
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9 4. Conclusions

10 Linear low density polyethylene (LLDPE) makes up (in particular) alongside polyolefin plastics (in
11 general) a large proportion of plastic solid waste (PSW). The accumulation of solid waste, namely
12 plastics, has been associated with various environmental burdens, in addition to, large economic loses.
13 In this manuscript, virgin LLDPE was subjected to pyrolysis in a fluidised bed reactor (FBR) pilot-plant
14 with both sand and Magnofil BT 80 catalyst as bed materials. The pyrolysis oil and wax products were
15 extracted at an average bed temperature of 600 and 700°C, and were also experimentally studied
16 accordingly. The oil yield decreased between 600 (8.7 wt.%) to 700°C (8.1 wt.%) in a reverse effect
17 with reaction time. This was attributed to the increase in the polyolefin polymer matrix's vibration, as
18 a result of the absorbed thermal energy with the increase in temperature. The experiments at 700°C
19 showed no wax formation but high yield of gaseous products and oils which are more lucrative in
20 managing accumulated plastic waste, which polyethylene constituents' large proportions of via thermo-
21 chemical conversion technologies. The estimated calorific value at 600°C was 45.5 MJ kg⁻¹ which is in
22 the acceptable range for both diesel and gasoline fuel market specifications. The sulphur content in the
23 pyrolysis oil was estimated as 0.013% and didn't get affected by change in temperature of the fluidised
24 reactor. However, de-sulphurisation will be required in the future to have the oil within acceptable
25 ranges of clean fuels. In addition, and to support this work's results in obtaining fuels from such
26 feedstock materials; the fuel range hydrocarbons were also analysed. The diesel fuel lumped
27 hydrocarbon range (C₁₀-C₁₉) was between 37 to 60% in the pyrolysis oils examined. It is therefore
28 concluded that the pyrolysis oil product in this work extracted at 700°C could be further refined to be
29 considered as a diesel fuel substitute after compliance with market standards. The oil extracted at 600°C
30 could be refined and considered as a gasoline product. The results determined experimentally from the
31 pilot-plant work herein are quite promising for sustainable fuel integration plans in the near future,
32 namely with existing petroleum refining complexes. It is also in compliance with future strategies the
33 world over for paving the way for circular economy and replacing linear one, namely in regions such
34 as the GCC.
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57
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59
60

1
2
3 Senior Research Technician after a fruitful and prosperous 33 years career at KISR ending his work
4 with duties assigned to this project.

5
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8
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11
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13 Preparation, M. van H.; Final Draft Review, H.J.K.; Experimental Analysis, A.H.; Final Draft Review,
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15 Review, A.C.; Final Draft Review.

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List of Figures

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2 Figure 1. Pilot plant picture used in this work showing in figure (a): 1. Controllers and SCADA, (2) Conveyer belt reaching to feeding hopper and
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4 arrangement, (3) FBR - Casing furnace and bed, (4) Cyclones and (5) Gas trap; and in figure (b): (6) Cyclone #1, (7) Cyclone #2, (8) Gas feed, (9) Weighing
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6 balance, and (10) Condenser. Image source Salahudeen et al. (2022) reprinted with permission.

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9 Figure 2. Product mass balance with respect to average reactor bed temperature ($^{\circ}\text{C}$). Products from 500°C were not analysed in this work as focus is on
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11 pyro-oils obtained but shown here for the reader's consideration in this section.

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14 Figure 3. Pyrolysis Oil and Wax Calorific Value (MJ kg^{-1}) as a Function of Average Reactor Bed Temperature ($^{\circ}\text{C}$).

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17 Figure 4. Fuel Potential Estimated for the Pyrolysis Oil and Wax Samples.

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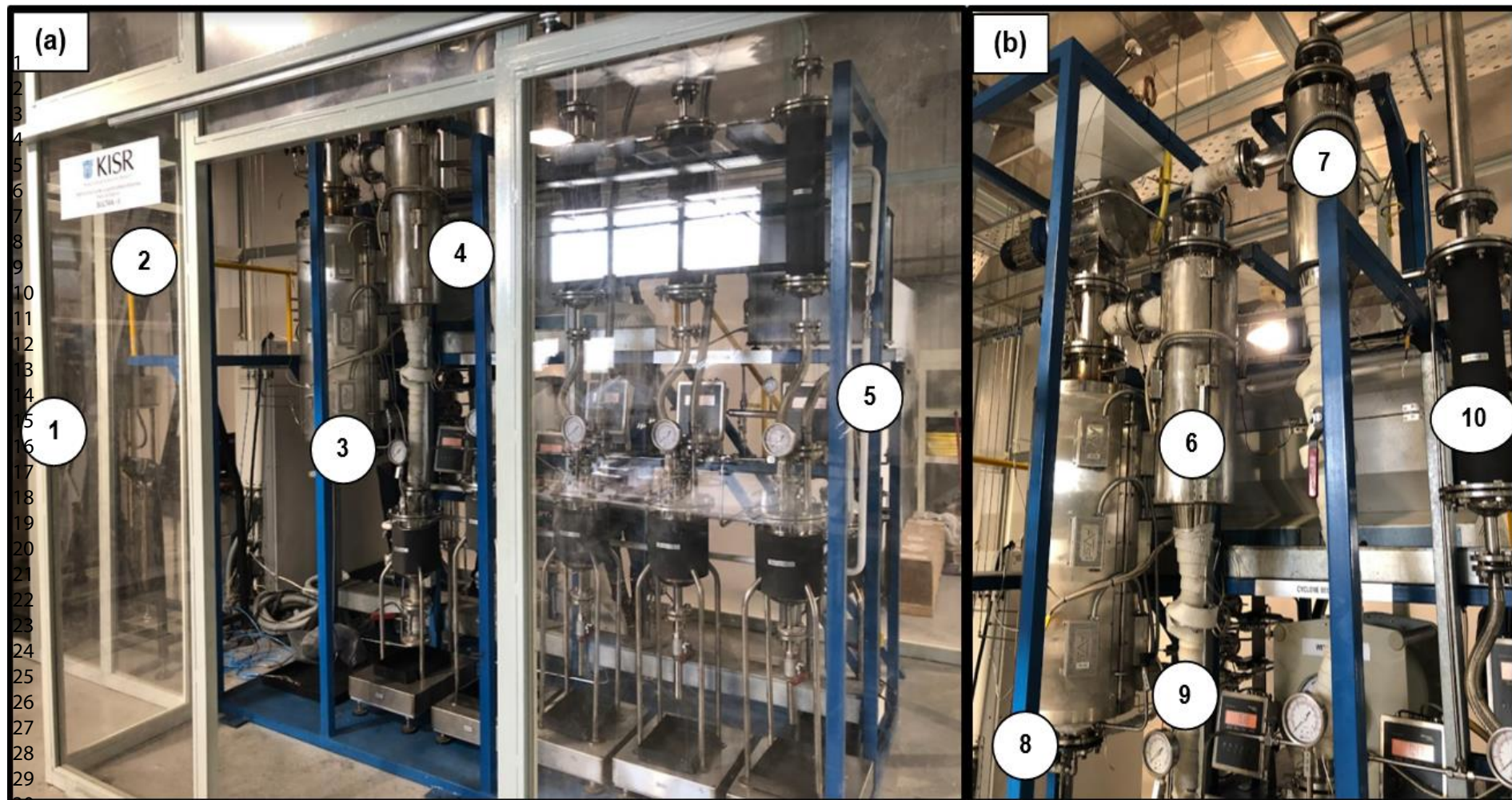


Figure 1. Pilot plant picture used in this work showing in figure (a): 1. Controllers and SCADA, (2) Conveyer belt reaching to feeding hopper and arrangement, (3) FBR - basing furnace and bed, (4) Cyclones and (5) Gas trap; and in figure (b): (6) Cyclone #1, (7) Cyclone #2, (8) Gas feed, (9) Weighing balance, and (10) Condenser. Image ACS Paragon Plus Environment

source Salahudeen et al. (2022) reprinted with permission.

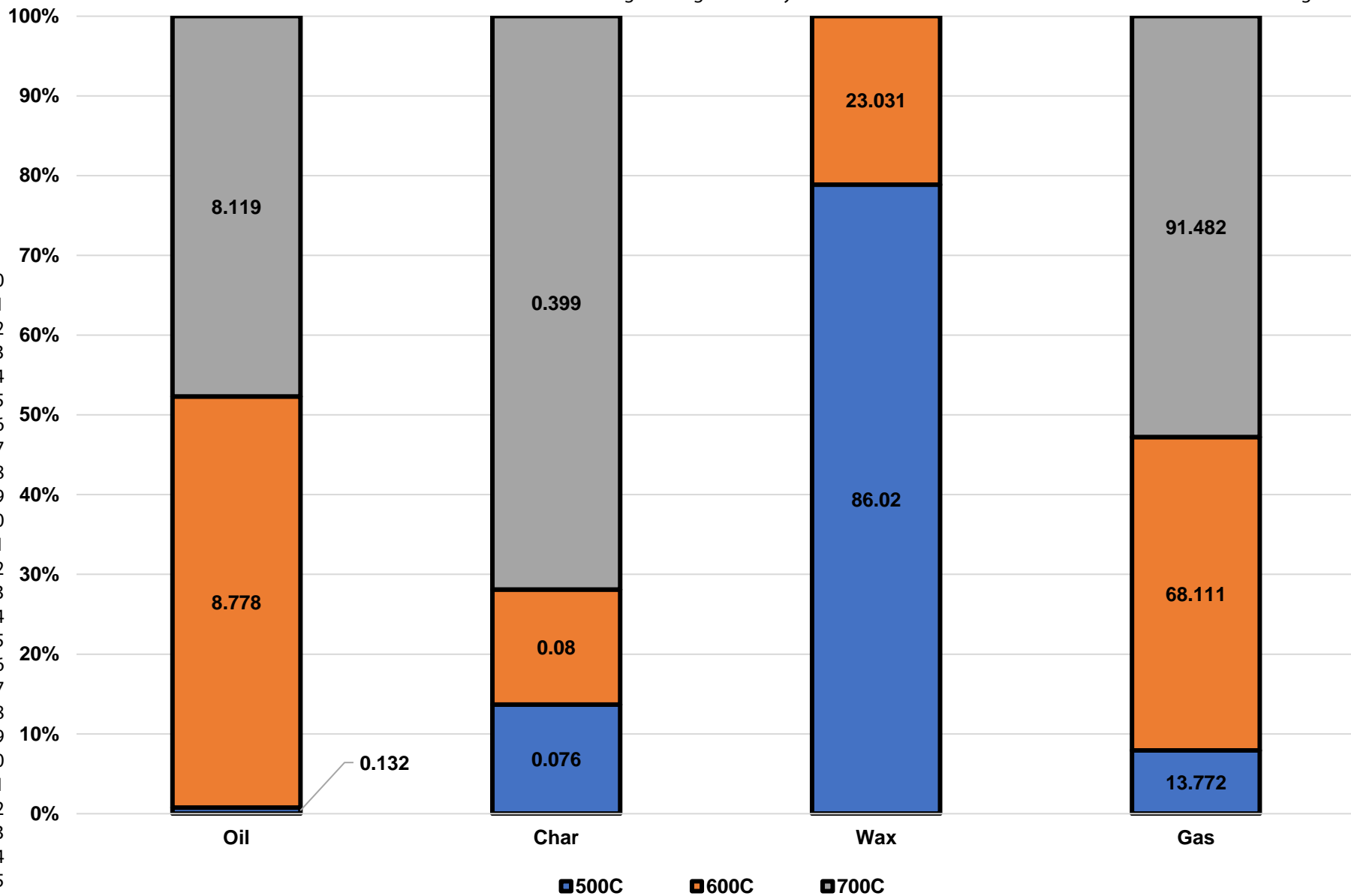


Figure 2. Product mass balance with respect to average reactor bed temperature (°C). Products from 500°C were not analysed in this work as focus is on pyro-oils obtained but shown here for the reader's consideration in this section.

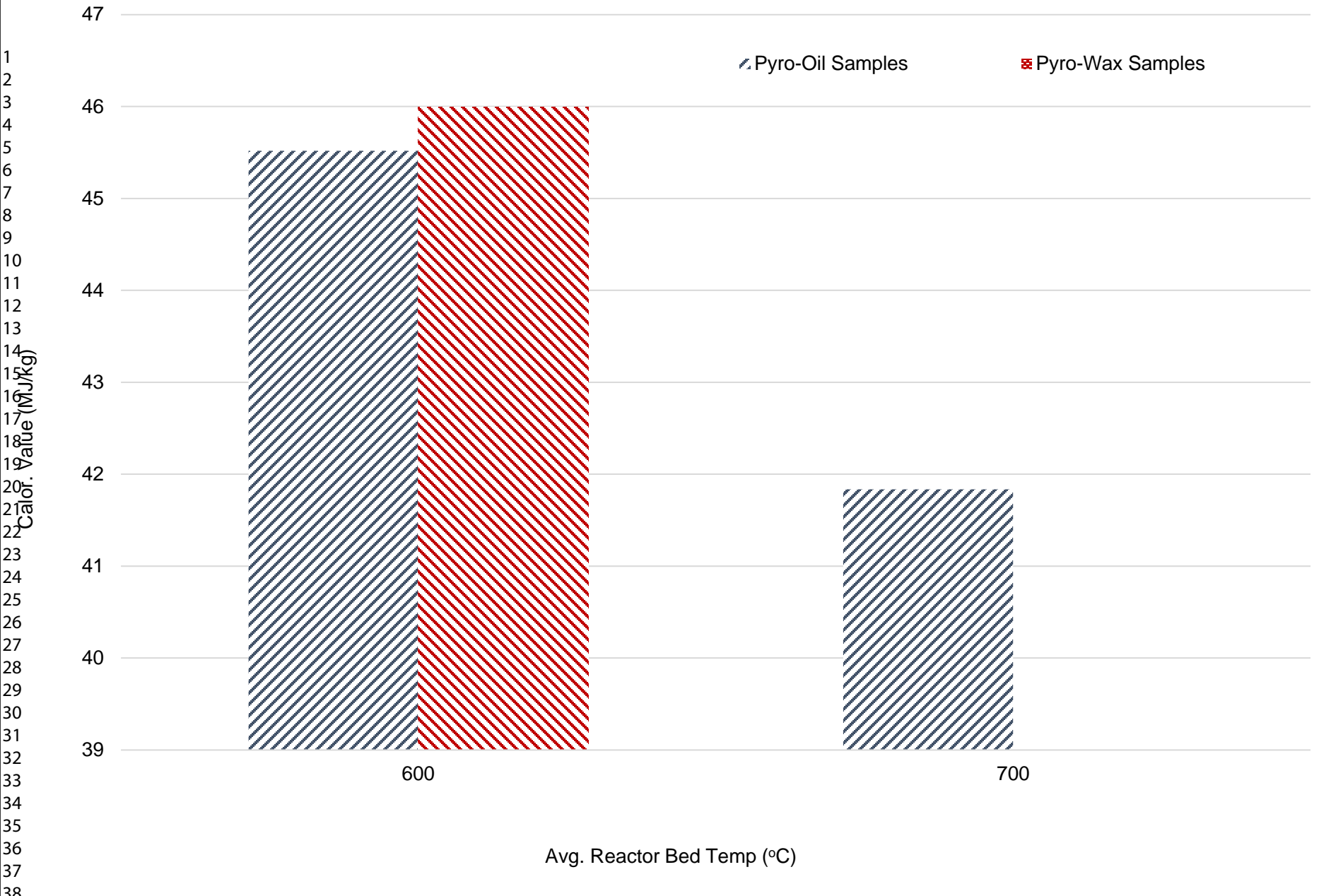


Figure 3. Pyrolysis Oil and Wax Calorific Value (MJ kg⁻¹) as a Function of Average Reactor Bed Temperature (°C).

■ C6-C9

■ C10-C19

■ C19+

Fuel Range Identification (%)

70
60
50
40
30
20
10
0

Pyro-Oil (600C)

Pyro-Oil (700C)

Pyro-Wax (600C)

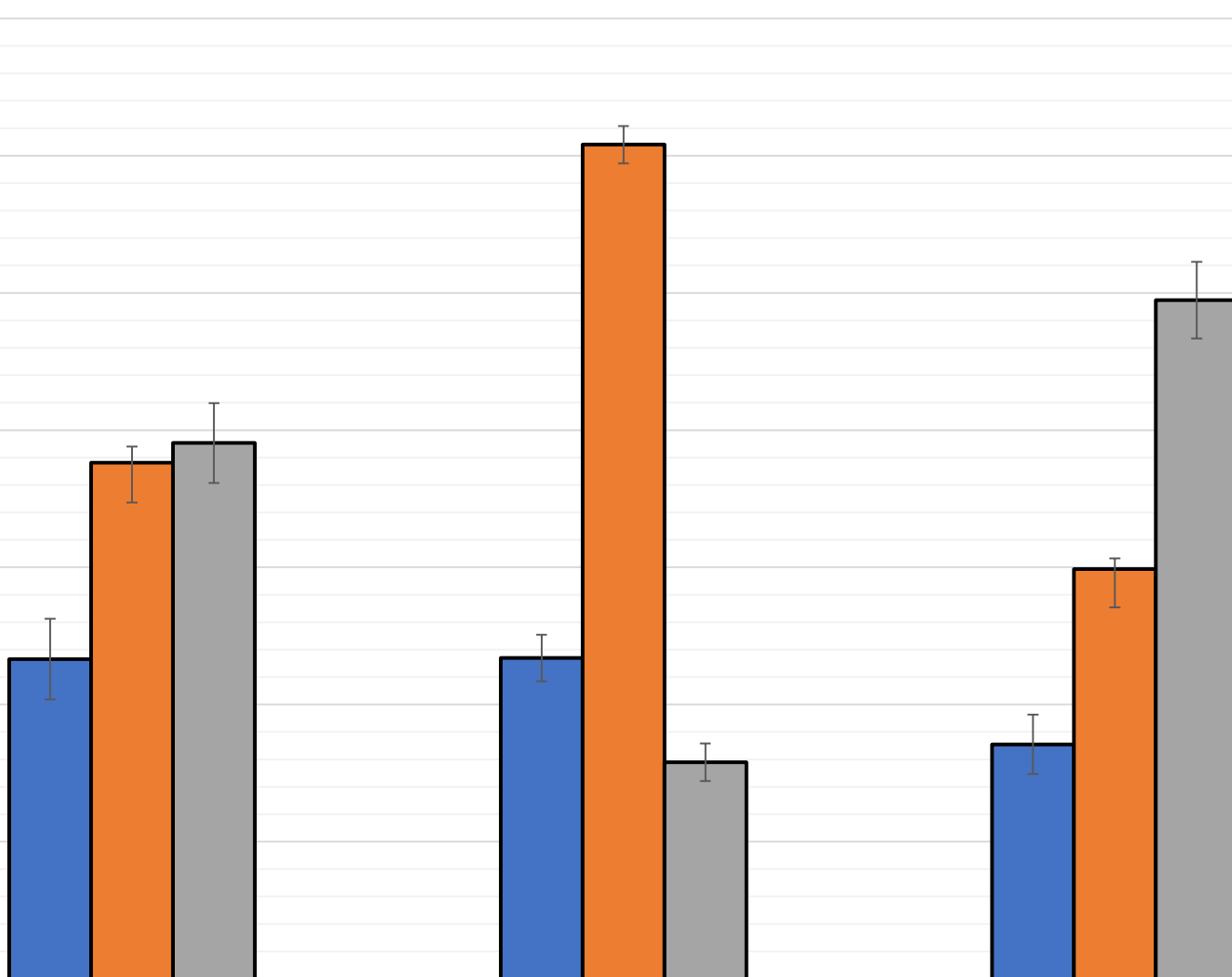


Figure 4. Fuel Potential Estimated for the Pyrolysis Oil and Wax Samples.