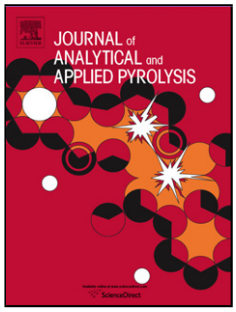

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Reverse engineering of plastic waste into useful fuel products

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Highlights

- Fast vaporization of the pyrolysis process lasted for about five minutes which was detected between the 35th and 40th minutes.
- Thermal pyrolysis enhances the yield of liquid oil at high degradation temperatures.
- Silica alumina catalyst favours the formation gaseous fractions at low temperatures.
- Pyrolytic liquid oil from high density polyethylene and polypropylene are of high quality and can be used individually or blended with conventional fuel as an energy source.

Abstract

This paper's twofold aims are: to assess the potential of converting plastic waste into useful fuels in both continuous and batch pyrolysis reactors using an appropriate technology and to investigate the effect of silica-alumina catalyst on the yield and quality of pyrolytic liquid oil. The plastic waste used (HDPE, PP and PS) were obtained from Kiteezi landfill site, Kampala (Uganda). In a further step, the properties of the liquid fuel obtained from pyrolysis were also compared with commercial transportation fuel to ascertain its suitability on diesel engines.The fuel qualities were analysed using ASTM standard test methods. At a degradation temperature of 450^{o}C, thermal pyrolysis in a batch reactor resulted in the highest yield of liquid fractions. The liquid yield of HDPE, PP and PS was found to be 80%, 82.6% and 80% by mass, respectively. In contrast, silica-alumina catalyst to feedstock ratio of 1:10 was the most effective in terms of gaseous fraction production. The gaseous fractions were: 60 wt% for the mixture, followed by HDPE (59.63 wt%), PS (59.07 wt%) and PP (49.33 wt%). A catalyst/polymer ratio of 1:10 greatly reduced the degradation temperature. The degradation temperature for HDPE, PP and PS was reduced by about 33%, 23% and 17%, respectively. The liquid oils from HDPE and PP had densities of 0.796 g/cm^3 and 0.786 g/cm^3; kinematic viscosities of 2.373 mm^2/s and 2.115 mm^2/s, dynamic viscosities of 1.889 mPas and 1.856 mPas; boiling point ranges of 119-364^{o}C and 148-355^{o}C; and cetane indices of 46 and 63, respectively. The characteristics of HDPE and PP pyrolytic sample oils are similar to conventional transportation fuel.

Keywords: Plastic waste; pyrolysis; appropriate technology; silica-alumina; liquid oil

1. Introduction

Plastics and their uses are part and parcel of modern daily life. The world's annual consumption of plastic materials was five million tonnes in the 1950's. Currently, the global production of polymeric materials has increased rapidly to 311 million tonnes [1]. Thus, more than 62 times polymeric materials are produced today than 60 years ago. The increased production of polymeric materials can be attributed to the rapid increase in world population which has coincided with economic growth and higher pursuit of life [2]. Other drivers responsible for the steady growth of plastic materials are its low density, user-friendly design, and low costs [3,4]. Plastics are widely used in phones, packaging, constructions, and automobiles. It is evident that plastics bring numerous societal benefits and offer prospects in technological and medical developments. However, the consequence of increased production and consumption is the generation of a large amount of plastic waste. Also, more resources are needed to meet the increased demand of plastics. The production of plastics requires unsustainable petroleum-based raw material inputs for their production. About eight percent (8%) of the total world crude oil production is used as both a feedstock and an energy source for the production of plastics [5]. Packaging polymeric materials which constitute more than 30% of the current production are rapidly discarded. With the decline of fossil fuel reserves, and finite capacity for disposal of waste to landfill, the current usage of plastics is simply unsustainable [6]. Ever since their inception, indiscriminate disposal of waste plastics has caused environmental problems globally [3], and many local, regional, and national authorities have begun taking actions [7].

Waste plastics are now a major stream in municipal solid waste (MSW) due to their increased production and usage. Currently, plastic wastes constitute about the third highest percentage in MSW after food and paper wastes in most cities [8]. Due to the increased demand and usage of polymeric materials as shopping bags, packaging materials, polyethylene terephthalate (PET) bottles and electrical appliances, most developing cities with even very low economic growth such as Kampala are producing more plastic wastes.

The problem of plastic waste is particularly serious in developing cities due to lack of integrated solid waste management coupled with their unique set of socio-economic, widespread poverty, and environmental injustice. Most of the generated waste plastics are neither collected nor properly disposed of causing littering and choking of gutters. For example, Jambeck et al. [6] reported that about 4.8 to 12.7 million metric tonnes (MT) of plastic wastes entered the ocean along coastal countries in 2010. At these alarming levels of plastic waste generation, countries with no or little capacity to recycle plastics face environmental challenges such as soil and water pollution, heavy metal pollution, and waterway blockage [9]. Injuries and deaths of aquatic animals, breeding ground for mosquitoes, blocking storm drains and sewage systems, leading to flooding and widespread of diseases are among the environmental problems associated with the improper disposal of waste plastics [3,7].

In Kampala, only two percent of about 62,050 tonnes of waste plastics generated annually are recycled into products such as bags, cones and fencing poles [10]. It is also estimated that about 3,000 tonnes of plastic wastes are dumped into soils annually. This affects soil and agricultural productivity, which is a backbone of the national economy. In addition, more than 60% of stray cattle deaths in Uganda are caused by consumption of polyethylene bags [11]. Unique sets of solutions are needed to solve this complex problem. Most plastic wastes are separated into PET, low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), polystyrene (PS) and polyvinyl chloride (PVC). These waste plastics pose serious environmental challenges because of their huge quantity and disposal problem as thermoplastics do not biodegrade for a very long time [12]. Currently, plastic waste is predominantly incinerated and landfilled or openly dumped in Uganda. These methods of plastic waste management have negative effects. This is because the former produce several pollutants that are harmful to the environment and the latter has the danger of leaching and soil impregnation, leading to the contamination of underground waters [13].

These environmental problems coupled with low-grade application of recycled plastics have led to research into alternative processes for plastic waste recycling. One of the most attractive of these alternatives, is the pyrolysis of plastic waste into useful fuels (gas and diesel) [14–16]. It is suggested that pyrolysis technology may be an appropriate solution to the problem of environmental pollutions that arise from landfilling or incineration of plastic waste [17]. Recycling of plastic waste via pyrolysis involves thermal degradation of the polymeric material at higher temperatures in the absence of oxygen to produce useful fuels. The decomposition process is usually carried out at temperatures between 400-500^{o}C [18,19]. The products of pyrolysis of plastic waste are liquid, gas, wax and char [20–22]. The proportion of each product depends primarily on temperature. Other factors include the plastic type, presence or absence of catalyst, reactor type and heating rate [13,23,24]. Catalyst plays a crucial role during the pyrolysis of plastic waste and also the modification of pyrolytic pathways [25]. It is reported that the quality of distillates which makes it suitable for many applications is increased when catalyst is added [26]. It is suggested that plastic-based diesel (PBD) can be used as an alternative source of energy due to its similar physicochemical properties to that of conventional fuel [27,28].

In this study, the performance of both the batch and continuous reactors for the pyrolysis of HDPE, PP and PS were evaluated. The study also examined the effect of silica-alumina catalyst on the yield of various pyrolysis products. The properties of the liquid fuel obtained from pyrolysis were also compared with commercial transportation fuel to ascertain its suitability on diesel engines.

2. Materials and methods

2.1 Source of plastic waste

In this study, plastic waste was collected from Kiteezi Landfill site. The Kiteezi Landfill site is the biggest and best-managed landfill site, located East of Kampala, Uganda. It is an 8-hectare site which is located about 12 km from the city center of Kampala. It is the main landfill site that receives waste from about 1.5 million inhabitants. Rapid population growth, which is caused by immigration, urbanization and the natural increase, has resulted in the generation of a large amount of wastes including plastics in Kampala. The composition of plastic waste from Kiteezi landfill site are grouped into PE, PP and PS. Sorting out, washing and shredding were the pre-treatments carried out. These pre-treatments were carried out to reduce contamination,

and to also get a better oil yield [29]. Similarly, tags and labels were removed to eliminate any influence on the liquid product. Fig. 1 is an illustration of the shredded plastic waste used in this study.

a. Plastic waste after washing b. Plastic waste after shredding

Fig. 1. Sample plastic waste after pre-treatment used in the study experiments.

2.2 Pyrolysis of HDPE, PP and PS to produce useful fuels

2.2.1 Temperature profile during plastic waste pyrolysis

The pyrolysis process was carried out in a processor designed and fabricated by University of Kentucky Appropriate Technology and Sustainability (UKATS) research team. The UKATS processor was conceived using an appropriate technology (AT). It was designed to be locally built in developing countries with local materials. It is simple in design, and does not require electricity for its operation. This makes it more suitable to be used in developing cities where most households depend on wood fuel for primary energy consumption. The components of the pyrolysis unit are the rocket stove (ensures efficient transfer of heat), pyrolysis reactor, and distillation pipes (see Fig. 2). Water cooled condenser was used as an auxiliary part of the reactor for air cooling [18]. The rocket stove is also made of mild steel and has the following dimensions: internal diameter of 38 cm and a height of 88 cm. The continuous reactor is made of mild steel and has the following dimensions: the total height of the reactor is 42.5 cm, the height of the conical section is 15 cm and the angle of the conical section is 27^{o}.

One kilogram (1 kg) of HDPE chips were measured and loaded into the reactor, which was then placed into the heating zone of the rocket stove before the fire was started heating. When the pyrolysis process started, the plastic waste melted and decomposed at high temperatures. The gases that were produced passed through the distillation pipes and into the water cooling condenser. Two thermocouples, 1 and 2 were used to measure the outer wall and inside temperatures (T1, T2) of the continuous reactor, respectively. The measurement of temperatures was done at a time interval of 5 min. The process ended when no more products came out. Liquid fuel was then collected over water using the principle of oil been less dense than water.

In order to study temperature variations during the pyrolysis process, a separate experiment was carried out without sample feed (empty reactor) under similar conditions. In the experiments, the temperature and the liquid fuel mass were recorded after the process.

Fig. 2. Pyrolysis experimental set up at Makerere University Agricultural Research Institute, Kabanyolo, Uganda.

2.2.2 Thermal and catalytic pyrolysis of HDPE, PP and PS

As different types of plastic behave differently in a pyrolysis process, post-consumer plastics in the form of HDPE, PP and PS were investigated in both the batch and continuous pyrolysis reactors. 500 g of each sample feed was used in this experiment. The pyrolysis reactor was then placed into the reaction chamber of the rocket stove. The firewood in the combustion chamber was ignited to provide energy for the pyrolysis process. There was a gradual increase of temperature until a temperature range of 330^{o}C– 350°C was obtained which was then maintained for about two hours before it was increased to about 450^{o}C until the completion of

the process. This is because rapid increase in temperature and temperatures beyond 450^{o}C could lead to increased production of wax and temperatures below 300^{o}C would lead to incomplete melting of the feedstock thereby increasing char, the residue remaining in the pyrolysis reactor [19]. The experiment was left to run until no further product was collected. On average, it takes about four hours for total completion of the process. The waste plastics melted and cracked to release hot pyrolysis vapors. These hot vapors passed through the distillation pipes and were collected over water using the concept of diesel being less dense than water. The liquid fuel was weighed at the end of the experimental process to obtain its mass (m_1).

The experimental procedure was repeated for catalyst/polymer ratio of 1 to 20 and 1 to 10. Each experimental run was repeated three times and results recorded did not vary by 3%. The maximum temperature of each polymer type during the thermal and catalytic cracking process was also recorded.

2.2.3 Mass balance analysis

The mass analysis of this technology basically involves the conversion of waste plastics through melting and cracking to produce liquid oil, gas and a solid residue. The estimation of yield of liquid oil and solid residue fractions was based on mass. Total conversion in terms of percentage was estimated using Equation 1. The percentage yields of liquid product, solid residue and gaseous product were calculated using Equations 2, 3 and 4, respectively [30].

$$\%\ conversion = \frac{m - m_2}{m} \times 100 \quad (1)$$

$$Liquid\ \ yield\ \ (L\ wt\%) = \frac{m_1}{m} \times 100 \quad (2)$$

$$Char\ \ yield\ \ (C\ wt\ \%) = \frac{m_2}{m} \times 100 \quad (3)$$

$$Gas\ \ yield\ \ (G\ wt\ \%) = 100 - (L + C) \quad (4)$$

Where,
m=mass of sample feed (g)
m_1=mass of liquid product (g)
m_2=mass of solid residue/char (g)

2.3 Characterization of pyrolytic liquid fuel

The fundamental properties such as density, viscosity, cetane index and distillation range of diesel fuels were analyzed in this study.

2.3.1 Density

Density measurement was determined according to ASTM 1298 [31]. The sample oil was brought to a temperature of 15^{o}C. The sample was then transferred to a hydrometer cylinder which was also brought to 15^{o}C. The hydrometer was then lowered into the test portion and allowed to settle. Hydrometer reading was measured and recorded with the temperature at equilibrium.

2.3.2 *Kinematic and dynamic viscosities*

For viscosity determination, an approximately 10 mL of pyrolytic sample oil was introduced into a viscometer (capillary tube). The viscometer was clean, dried and previously calibrated. The capillary tube was immersed in a thermostatic bath. The temperature of the bath did not vary more than 40±0.02ºC [32]. A vacuum pump was employed to draw sample oil until it reached the upper meniscus in the viscometer tube after the stabilization of temperature in the bath (approximately 40 minutes). A stop watch was used to count the flow time between the upper and lower meniscus. After the determinability of the test of each sample, the kinematic viscosity was obtained using Equation 5 (ASTM D445) [33]. The average value of readings of time was ±0.20%. The dynamic viscosity was subsequently estimated using Equation 6.

$$v = Ct \tag{5}$$

Where,
v=kinematic viscosity (mm^2/s)
C=viscometer calibration constant (mm^2/s)/s
t=flow time (s)

$$\eta = \rho v \tag{6}$$

Where,
η= dynamic viscosity (mPas)
ρ= density (kg/L)

2.3.3 *Distillation*

Distillation of the samples was performed in Herzog HDA-620 automatic atmospheric distillation following ASTM D86 at ambient pressure [34]. For the procedure, 100 mL of pyrolytic liquid fuel was transferred to a distillation flat bottom flask. The distillation flask was equipped with a thermocouple sensor. The flask was heated to keep a distillation ratio of 4 mL/min and 5 mL/min [32,35]. The distilled sample was condensed and collected in a measuring cylinder at room temperature. The distillation volume recovered at 250ºC, 350ºC and 365ºC together with initial and final boiling points were measured. The temperature at which the first drop of distillate was observed was recorded as the initial boiling point (IBP, ºC) whereas the temperature at which all the oil sample in the distillation flask evaporated was recorded as the final boiling point (FBP, ºC). Also, distillation temperatures at recovered volumes of 10%, 50%, 90% and 95% were recorded.

2.3.4 *Calculated cetane index*

The calculated cetane index (CCI) was estimated using the Four Variable Equation (ASTM D4737) [36]. The four variable equation is presented in Equation 7.

$$CCI = 45.2 + 0.0892\ T_{10N} + (0.131 + 0.901\ B)T_{50N} + (0.0523 - 0.420\ B)T_{90N} + 0.00049\ (T_{10N}^2 - T_{90N}^2) + 107\ B + 60\ B^2 \tag{7}$$

Where,
CCI=calculated cetane index

$$T_{10N} = T_{10} - 215$$

$$T_{50N} = T_{50} - 260$$

$$T_{90N} = T_{90} - 310$$

$$B = \left[\exp^{-3.5(\rho - 085)}\right] - 1$$

2.4 Data analysis

Data collected were analyzed to determine the effects of various treatments on the yield of product fractions using Microsoft Excel (2013 Edition). The analysis of variance (ANOVA) in dependent variables among the treatments was carried out first to check for the significance of treatments' effects. All statistical tests were done at an alpha value of 0.05.

3. Results and discussion

3.1 Temperature profile

Temperature is considered to be one of the most important factors during the pyrolysis of plastic waste since it dominates the cracking of the sample feed. The temperature variations in the reactor with and without sample feed are shown in Fig. 1 and 2, respectively. Fig. 1 shows large temperature gradient between the outer wall of the reactor and the space inside the reactor. The temperature inside the reactor was comparatively lower than the wall temperature during the first few minutes after the start of the experiment. This is because the furnace had just heated up and the heat that reached the pyrolysis reactor was low. After 35 minutes, higher rate of heat transfer occurred, where the wall and space temperatures of the pyrolysis reactor reached 136.5^{o}C and 119.0^{o}C, respectively. The maximum temperature gradient (100^{o}C) was observed after 70 minutes. This phenomenon is comparable to what was observed by other authors [37]. The sudden rise in space temperatures towards the reactor wall temperature from the 35th to 40th minute indicates the beginning of gas generation inside the reactor; which is an indication of vaporization. From the pyrolysis of HDPE, fast vaporization lasted for about five minutes from the 35th to 40th minute (shown in Fig. 1). The wall temperature approached a constant temperature of 350^{o}C; whereas the temperature inside the reactor approached a temperature of 283^{o}C.

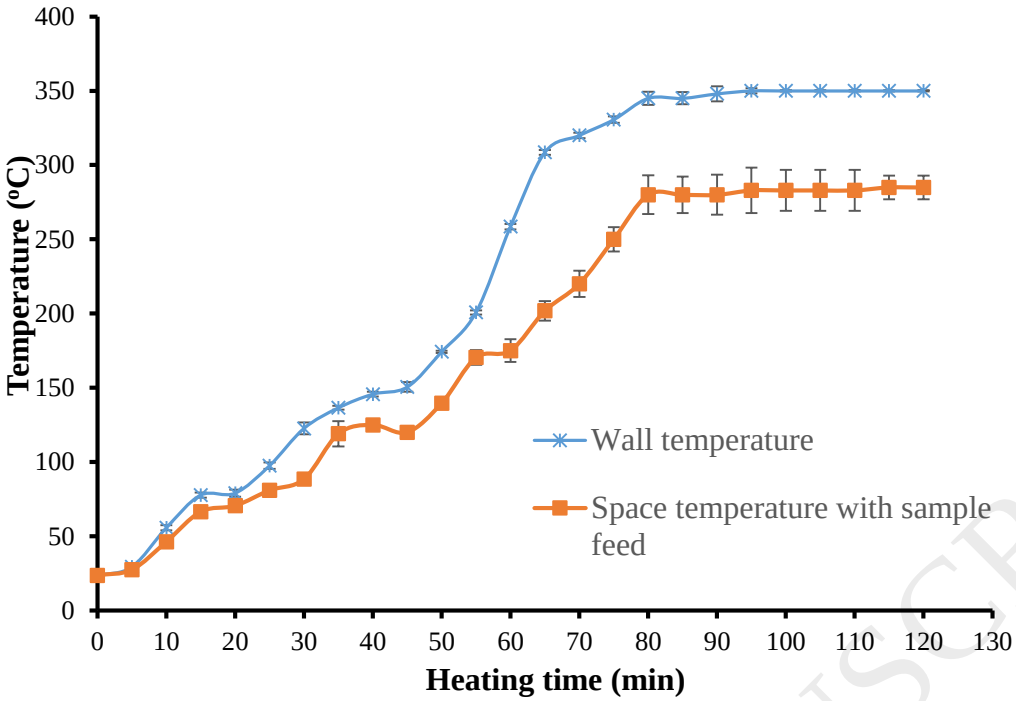

Fig. 3. Temperature profile of pyrolysis reactor with sample feed.

The heating rate for the experiment was considered to be 15 °C/min. Constant and early heating of sample feed was observed as compared to when the pyrolysis reactor was empty which shows a delay in temperature increase at the heating zone of the pyrolysis reactor. This result corroborates with the studies conducted by previous authors [38]. According to Singh & Ruj [38], lag in temperature rise observed at the heating zone is due to the absence of sample feed in the reactor, as air heats up slower than the sample feed in the reactor. The space temperature of the pyrolysis reactor increased slowly up to 70.5 °C and a sudden temperature rise was observed between 30-80 minutes where the pyrolysis reactor reaches the optimum temperature range when there was no sample feed as shown in Fig. 4. However, the presence of sample feed inside the reactor promotes a rapid increase in temperature after few minutes of the experiment. This is because the sample feed absorbs heat to increase the temperature of the pyrolysis reactor. The sample feed gradually melts down and gain consistent temperature which helps to heat up early by gaining temperature and subsequently breaks down into smaller hydrocarbons. This phenomenon was different from observations made by Gao [39] because of the higher quantity of sample feed considered for this study (1000.0 g compared to 10.0 g).

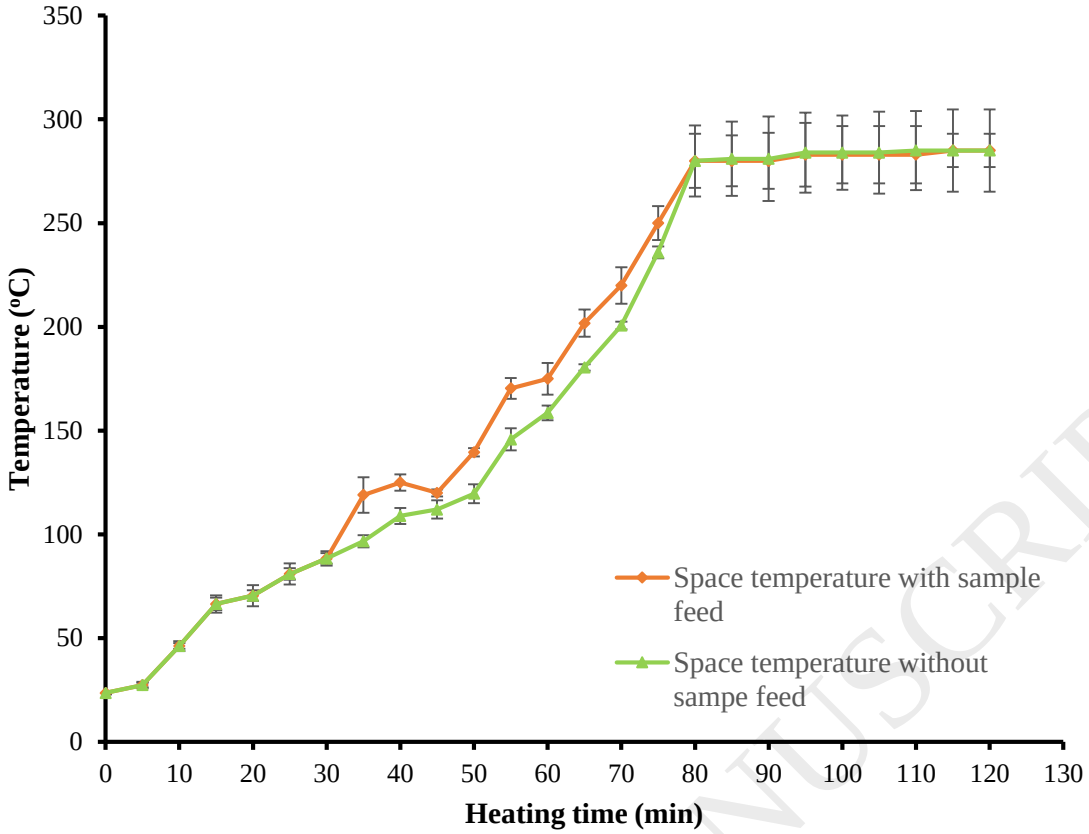

Fig. 4. Temperature profile of pyrolysis reactor with and without sample feed.

Getting to the completion of the pyrolysis process, there was a simultaneous increase in temperatures of the outer wall of the reactor and the outflow vapors. This results in loss of heat because the outflow vapors carry a significant amount of heat along which ends up heating the distillation pipes and the condensation system. Thus, the space temperature curve of sample feed becomes lower than the space temperature of the empty reactor.

3.2 Thermal and catalytic pyrolysis of HDPE, PP and PS

The effect of silica alumina catalyst on degradation temperature during pyrolysis of HDPE, PP and PS was investigated. Fig. 5 presents the maximum degradation temperature observed during the pyrolysis experiment. ANOVA results indicate that silica-alumina catalyst and polymer type have significant effects on the degradation temperature. The P-values computed for catalyst and polymer type are 0.040 and 0.049, respectively.

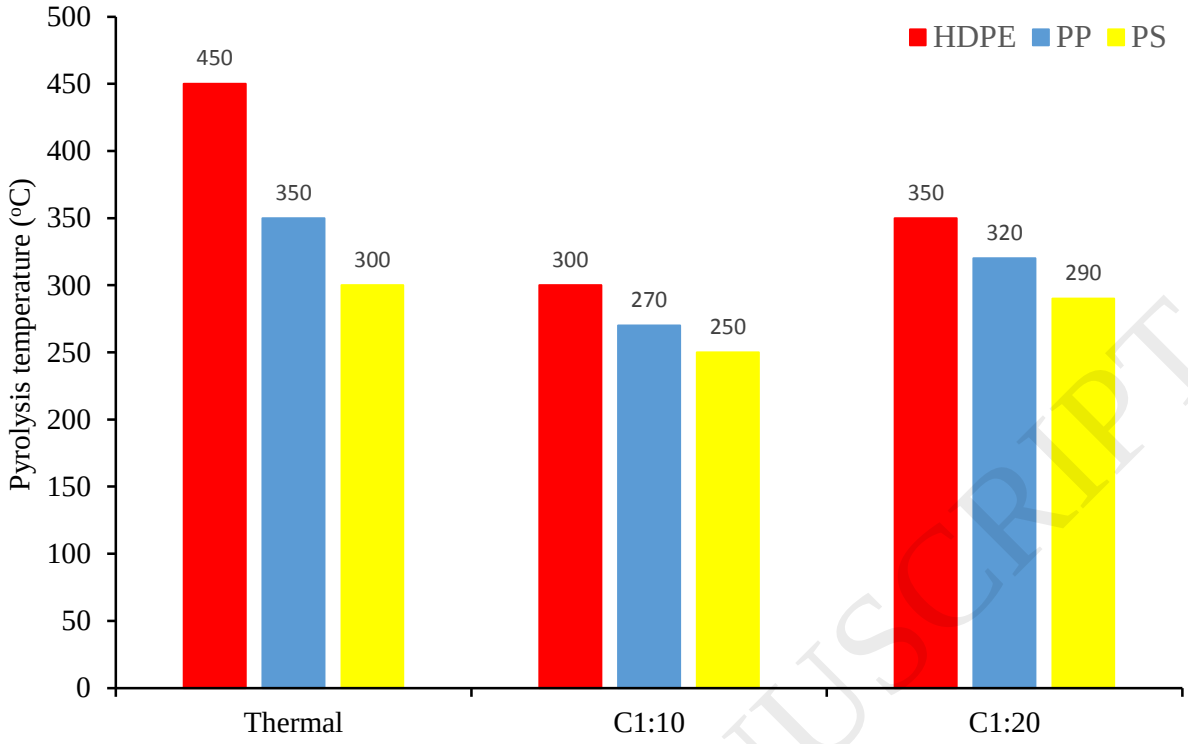

Fig. 5. Temperature of maximum degradation for HDPE, PP and PS with and without catalyst.

Thermal decomposition of HDPE was observed to be the highest, at around 450°C, while PP and PS were degraded at 350°C and 300°C, respectively. A similar observation was made by Marcilla et al. [40]. The authors reported the degradation of HDPE to be the highest and it was observed at 467°C. It was reported in their study that higher temperatures required by HDPE during pyrolysis are caused by the unstable nature of tertiary carbons in the thermal behavior of the HDPE carbon chain. It is reported in literature that due to the higher activation energy associated with HDPE (than PP and PS), higher temperatures are required during the pyrolysis of HDPE to break the carbon chains to improve the yield of various fractions [41,42]. In this study, the thermogravimetric behavior of all polymers was strongly influenced when silica-alumina catalyst was employed. This effect can be explained by the highly acidic nature and easy accessibility of acid sites in silica-alumina catalyst. As shown in Fig. 4, the change measured to lower temperatures was different, which was dependent on the catalyst to feedstock ratio. It is worth mentioning that the use of catalysts play a significant role during the process of pyrolysis. Thermal pyrolysis requires more energy than is needed in the presence of catalysts. A catalyst to feedstock ratio of 1:10 caused the highest change in temperature (100°C in HDPE, 80°C in PP and 70°C in PS). A catalyst to feedstock ratio of 1:20 resulted in the lower activity towards HDPE (50°C). From an energy conservation point of view, a catalyst to feedstock ratio of 1:10 is the most suitable.

3.3 Continuous vs batch pyrolysis

The effects of continuous and batch reactors on liquid, gas and solid residue fractions were investigated. As shown in Fig. 6, complete conversion of PP and PS was observed when the batch reactor was used.

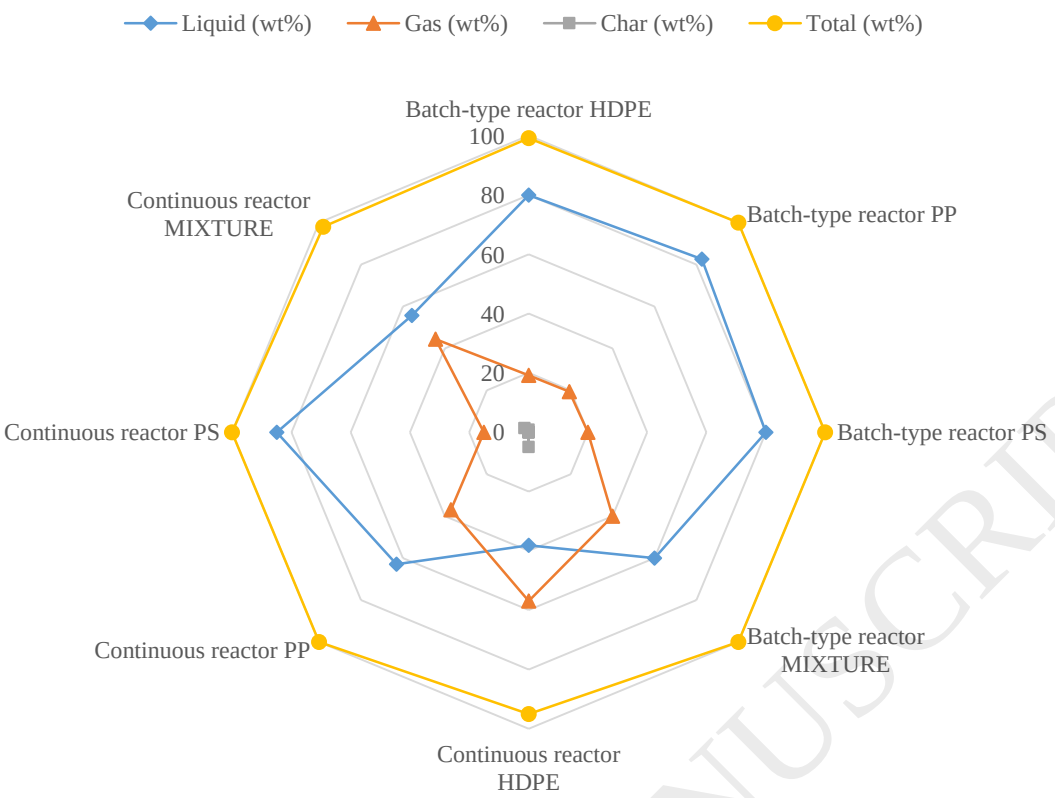

Fig. 6. Pyrolysis product yields in continuous and batch reactors during thermal pyrolysis

The marginal yield of char observed for all sample feed was in the form of tiny particles and fine powder at the bottom of the reactors. The formation of char during pyrolysis of waste plastics is a well-documented fact, which has been previously studied and reported by many researchers [43,44] and other authors [16,20]. The proportion of solid residue (which is mostly char) for PP and PS in both the continuous and batch reactors was insignificant. However, the yield of char was slightly higher in the continuous pyrolysis of HDPE than the batch pyrolysis (5 wt% higher than 2.8 wt%). The formation of char during pyrolysis is reported to be dependent on the molecular structure of polymer which increases with the presence of –OH and =O atoms [43]. These results corroborate with earlier research conducted by other researchers [45], where the yield of char from the pyrolysis of PP and PS was very minimal. Char produced from pyrolysis of plastic waste is reported to have a high calorific value [46]. This makes it suitable to be used as an energy source in boilers [47]. Similarly, char can be used as a raw material to produce briquette which can be used as primary energy source for cooking [48].

As can be seen from Fig. 6, the yield of liquid was significantly enhanced when the batch reactor was employed in all cases. The yield of liquid from the pyrolysis of HDPE, PP and PS were 80 wt%, 80.6 wt% and 80 wt% respectively. Conversely, the yield of gases was significantly higher in the continuous reactor. The results obtained in this study can be attributed to the fact that, continuous reactors operate at higher temperatures which promote the formation of gases. The gaseous yield of HDPE in the continuous reactor was the highest (61.7 wt%) followed by PP (37 wt%) and PS (14.7 wt%).

3.4 Effect of silica-alumina catalyst on the yield of product fractions

As can be inferred from Table 1, both polymer type and catalyst (both catalyst ratios) are significant factors that affect the yield of liquid fractions. P-values of 0.0002 and 0.0405 were calculated for catalyst and polymer types, respectively. Fig. 7 and Table 2 show the liquid yield and mass balance for the experiments in all cases, respectively. There was variation in the catalyst to feedstock ratio by changing the amount of silica-alumina catalyst used. The mean yield was calculated from three catalytic cracking runs conducted with each sample which did not differ by four percent. The yield of liquids was generally the main fractions in thermal pyrolysis, reaching 60-82.6 wt%. These results are in agreement with those observed by other authors [49] where the yield of liquid fraction in thermal pyrolysis reached 79.3 wt%, exceeding the yield observed when catalysts were used. The gaseous fractions were comparatively lower in thermal pyrolysis (17.2-20 wt%).

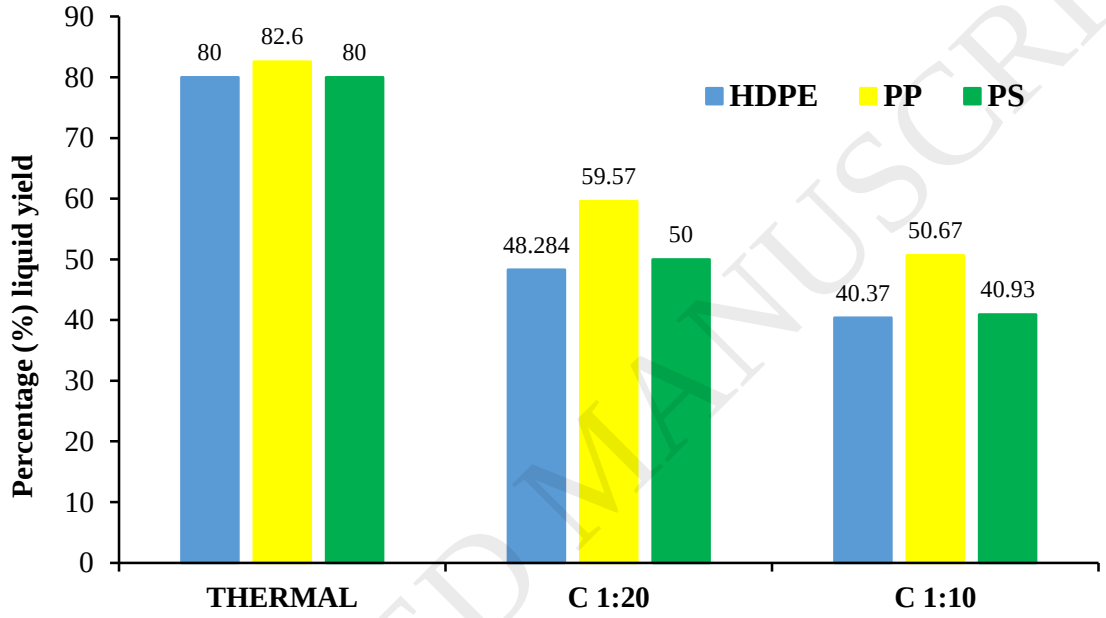

Fig. 7. Effect of catalyst on the yield of liquid fuel

Contrary, the production of gaseous fraction was greatly enhanced when silica-alumina catalyst was added. As can be seen in Table 2, increasing the amount of catalyst (i.e. catalyst/feedstock ratio of 1:10) results in an increase of gas production, but reduction of char formation is observed. This is because when more catalysts are used the sample feed become overloaded. This means that all the sample feed in the reactor get access to the surface of the catalyst resulting in fewer yields of char. This result is consistent with other researchers [40] which indicated that the presence of a catalyst decreases the yield of char. It is also well demonstrated from the data obtained (see Table 2) that the highest fraction of the gaseous product was obtained from the mixture of plastics in both catalyst to feedstock ratios. Although not within the scope of this study, data from literature indicates that gaseous fraction produced from the pyrolysis of waste HDPE is mainly made up of ethane and ethene [50].

The percentage decrease in the yield of liquid fractions is presented in Fig. 8. With a higher catalyst/feedstock ratio (1:10), there was a considerable reduction in the yield of liquid fraction. This result is consistent with other authors [51]. According to other researchers [51,52], higher amounts of gaseous fractions in the pyrolysis products is due to the strong acidity of silica-

alumina catalyst (increases with the amount of catalyst), which is characterized by enhancing secondary degradation of primary pyrolysis products to smaller molecules. It is worth noting that, increasing catalyst percentage enhances polymer conversion and also decomposes it further to yield smaller molecules.

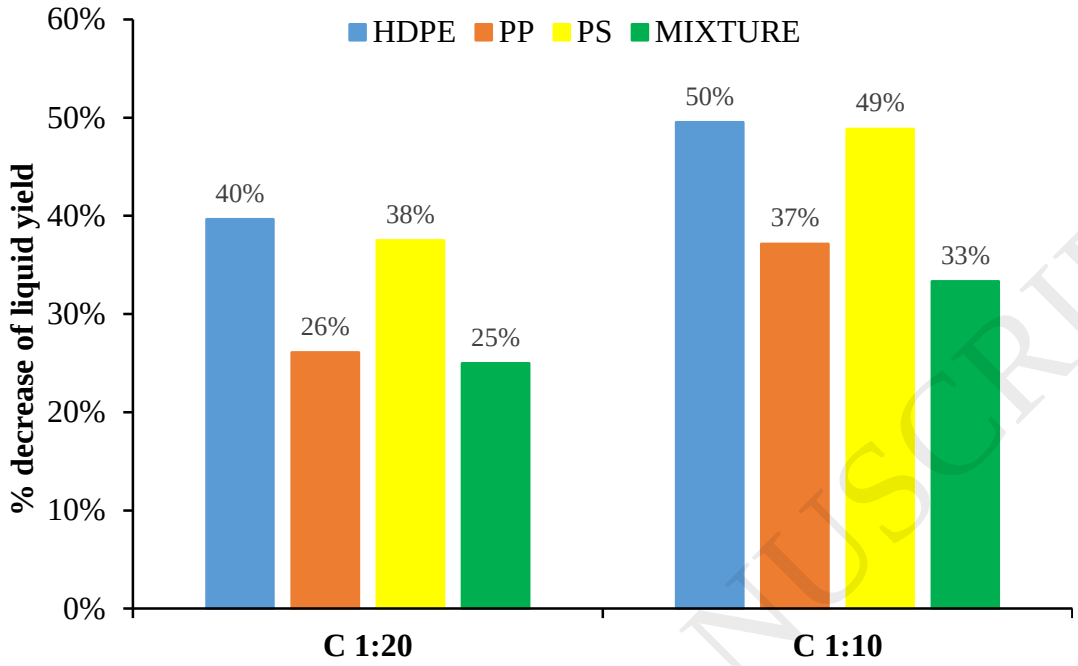

Fig. 8. Percentage decrease in the yield of liquid fuel

3.5 Physicochemical and fuel properties of liquid fuel

The liquid product obtained from the pyrolysis of HDPE, PP and PS was analyzed using American Society for Testing and Materials (ASTM) standard test methods. The appearance of the liquid fuel obtained from HDPE pyrolysis was light yellowish. The appearance of pyrolytic oil from PP was deep brown whereas pyrolytic oil from PS was dark yellowish. All the pyrolytic oils were free from visible sediments. Table 3 presents properties of reference diesel and pyrolytic sample oils.

Density is considered to be a very important property in petroleum products. The densities of liquid products obtained from HDPE, PP and PS were found to be 0.796 g/cm^3, 0.786 g/cm^3, and 0.894 g/cm^3, respectively. The density values for HDPE and PP are comparable with that of conventional diesel fuel and fall within the range of diesel and kerosene. Conventional transportation fuels can be used to blend with the pyrolytic fuel oil to modify the density. The density of PS pyrolytic liquid is a little higher than that of conventional transportation diesel.

For all the pyrolytic sample oil, the dynamic viscosity was found to be in the range of 1.291-1.889 mPas. This is in agreement with the value of 1.770 mPas, reported by other authors [53]. The structure and composition of the individual polymers contributed to the variation in their dynamic viscosities. It is also worth noting that, dynamic viscosity values estimated are also in agreement with the range of 1.00–4.11 mPas for conventional transportation diesel. Kinematic viscosity is also one of the most important fuel properties. This is because it dictates the spray pattern and atomization of injected fuel in a combustion chamber [53]. Highly viscous fuels lead to poor engine performance. According to Kim et al. [54], highly viscous oils are difficult

to transport to fuel supply system and atomizer. This makes the use of higher viscosity oils unsuitable during winter. On the other hand, the use of liquid oils with low viscosity results in severe pump and injector leakage. This reduces power output of an engine due to the reduction in fuel delivery. The kinematic viscosities of pyrolytic liquid oil from HDPE, PP, and PS were found to be 2.373, 2.115 and 1.461 mm^2/s, respectively. These kinematic viscosity values are similar to the values estimated by authors [53] and other researchers [46]. They estimated the kinematic viscosity of pyrolytic liquid oil from HDPE and PP to be 1.92-3.24 mm^2/s and 2.18 mm^2/s respectively. The dynamic viscosity of fuel oils from waste plastic is generally considered to be low. However, kinematic viscosity of pyrolytic HDPE liquid oil (2.373 mm^2/s) and pyrolytic PP oil (2.115 mm^2/s) falls within the range of 2-5.5 mm^2/s for conventional transportation fuels (Table 3). The kinematic viscosity estimated for pyrolytic PS liquid oil (1.461 mm^2/s) was below the standard range. This is in agreement with earlier studies [55]. The low kinematic viscosity indicates that high amount of gasoline and low amount of heavy oil is present in the pyrolytic oil. Therefore, PS pyrolytic oils must be blended with conventional transportation fuels before it can be used on engines.

From the distillation results presented in Table 3, the initial and final boiling points for HDPE sample oil were found to be 119^{o}C and 364^{o}C, respectively. Whereas, boiling point range of PP pyrolytic liquid oil is 148-355^{o}C. This observation is similar to the boiling range reported in other studies [56]. The distillation range obtained from their study was 58–376^{o}C. This boiling point range also falls into the range recommended being as a conventional fuel. According to Kumar et al. [57] and Kumar & Singh [58], the boiling range observed in both HDPE and PP pyrolytic oils indicates the presence of several oil fractions such as diesel, gasoline, and paraffin. From this result, it is detected that these could be possible feedstock for further upgrading or use of lighter compounds as a diesel fuel.

The cetane index gives a clear indication of the ignition quality of diesel fuel. The cetane indexes estimated for HDPE and PP derived fuels were 46 and 63, respectively. The cetane index obtained for HDPE pyrolytic sample oil is comparable to the results obtained by other researchers [58]. According to Ahmad et al. [30], higher cetane index is attributed to the presence of α-olefins and linear paraffin. Results from this study indicate that pyrolytic sample oils from HDPE and PP are enriched in these hydrocarbons. Also, these higher cetane index values are an indication of excellent combustion properties of the liquid fractions [59].

3.6 Potential application of pyrolysis oils

In Uganda, plastic waste is the third largest in MSW stream and is mostly landfilled. However, plastic wastes have the potential to be converted into liquid oil and other useful products. The results of density, kinematic viscosity, dynamic viscosity, distillation range and calculated cetane index obtained are comparable with conventional transportation fuel (see Table 3). Many researchers have used liquid oil from plastic waste; either alone or blended with conventional fuel as an energy source. Blends such as PO10 (10% plastic fuel and 90% conventional diesel in volume), PO20, PO25, PO30, PO50, and PO75 have all been used as an energy source on diesel engines. Kaimal & Vijayabalan [28] reported blend PO25 showed compatible results with conventional diesel at 1500 rpm. Also, in the studies of previous researchers [60], PO20 showed similar results with diesel in terms of energy, NO_x and CO emissions. Kalargaris et al. [61] investigated the use of pyrolytic liquid as primary energy source on the performance of diesel engines. The authors concluded that the addition of fuel

additive enhances brake thermal efficiency and lowers exhaust emissions. Lee et al. [62] reported that with the use of diesel engines, pyrolytic liquid oil can be used to generate electricity. However, properties of pyrolytic oil from PS (see Table 3) indicate that higher blends of conventional diesel may be required before they can be used as an energy source in diesel engines.

4. Conclusions

Thermal and catalytic reverse polymerization is attractive method of handling plastic waste. In the experiment, a large temperature gradient was detected to exist between the reactor wall and inside space of reactor. It was found that fast vaporization during cracking of HDPE in a continuous reactor lasted for about five minutes (between 35^{th} and 40^{th} minutes). Based on these findings, the presence of gas bubbles in the condenser can be used as an indicator to detect the beginning of the cracking process.

The results showed that for catalyst/polymer ratio of 1:10, liquid oils from HDPE, PP and PS were low. The degradation temperature for maximum conversion was also low; and was observed at 300^{o}C, 270^{o}C, and 250^{o}C for HDPE, PP and PS, respectively. The presence of silica-alumina catalyst favored the formation of gaseous fractions. The production of gaseous fractions increased from 17.2-20 wt% to 40.43-60 wt%. Thermal pyrolysis resulted in the highest yield of liquid oils for sample feed but at the highest degradation temperature. The degradation temperature observed during thermal pyrolysis of HDPE, PP and PS was 450^{o}C, 350^{o}C and 300^{o}C, respectively. The yields of oil fractions in batch pyrolysis were significantly higher than the continuous and at a lower pyrolysis temperature. The use of a batch reactor must therefore be encouraged to improve liquid yield

The liquid oil produced from HDPE and PP has densities of 0.796 g/cm^3 and 0.786 g/cm^3; kinematic viscosities of 2.373 mm^2/s and 2.115 mm^2/s, dynamic viscosities of 1.89 mPas and 1.86 mPas; boiling point ranges of 119-364 ^{o}C and 148-355 ^{o}C; and cetane indices of 46 and 63, respectively. The characteristics of HDPE and PP pyrolytic sample oils are similar to conventional transportation fuel. However, further processing must be carried out (especially for PS oil) before it is used in diesel engines. Furthermore, for full implementation of this technology in developing cities, detailed sustainability assessment on economic feasibility, environmental impact, and social acceptability must be conducted.

Availability of data

The data supporting the conclusion of this article is a Microsoft Excel file saved as "*Reverse engineering of waste plastics into useful fuel products_PAO_NB_AZ_JS_NK*".

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Tables

Table 1
ANOVA table for the effect of catalyst ratio on liquid fractions

Source	Sum of squares	DF	Mean square	F-value	P-value
Polymer type	382.5611	3	127.5204	5.2755	0.0405*
Catalyst	2330.6070	2	1165.303	48.2086	0.0002*
Residual	145.0326	6	24.1721		
Total	2858.2010	11			

*Significant difference

Table 2
Mass balance of plastic waste conversion into fuels

Catalyst/feedstock ratio	Feedstock	Liquid (wt%)	Gas (wt%)	Char (wt%)	Total conversion (wt%)
Thermal	HDPE	80	17.2	2.8	99.2
	PP	82.6	17.4	<0.3	100
	PS	80	20	<0.3	100
	MIXTURE	60	40	<0.3	100
C1:20	HDPE	48.28	51.72	<0.3	100
	PP	59.57	40.43	<0.3	100
	PS	50	50	<0.3	100
	MIXTURE	45	55	<0.3	100
C1:10	HDPE	40.37	59.63	<0.3	100
	PP	50.67	49.33	<0.3	100
	PS	40.93	59.07	<0.3	100
	MIXTURE	40	60	<0.3	100

Table 3
Fuel properties comparison of waste HDPE, PP and PS pyrolytic oil with commercial transportation fuels

Liquid fuel	Density (g/cm^3)	Kinematic viscosity (mm^2/s)	Dynamic viscosity (mPas)	CCI	IBP (ºC)	FBP (ºC)
HDPE pyrolytic oil	0.7960	2.373	1.8889	46	119	386
PP pyrolytic oil	0.7860	2.1152	1.8583	63	148	355
PS pyrolytic oil	0.884	1.4614	1.2919	-	128	179
Diesel	0.82-0.85	2-5.5	1-4.11		172	350
Gasoline	0.72-0.78	-			27	225
Biodiesel	0.88	4-6			315	350
Heavy fuel oil	0.94-0.98	>200			-	-
Test method	ASTM D1298	ASTM D445	ASTM D445	ASTM 4737	D86	D86