USE OF POLYETHYLENE AS A FEEDSTOCK FOR VALUE ADDED PRODUCT RECOVERY: WAX RECOVERY FROM PYROLYSIS

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ABSTRACT

One of the main engineering objectives nowadays is to develop and design a sustainable practice whilst operating a technology that can yield value added products and be environmentally friendly in the same time. No better example can be provided of ongoing research of such technologies other than waste to fuel and energy solutions. Such technologies can recycle solid waste whilst maintaining a sustainable practice and operation. A prime example of such is the technique of pyrolysis, where waste is deteriorated in inert environments and products of such process are used in the place of petroleum fossil-based ones. One of the products of pyrolysis namely when using a polyolefin polymer is chemical waxes that were proven recently as a valuable product on the market. These waxes have a potential of having fuel range hydrocarbons and their market is of growing capacity as of late. In this work, the pyrolysis of polyethylene (PE) sourced as a virgin extrusion grade and used a translucent pellets, was used to produce waxes in the pyrolysis operation of fixed bed batch type. The pyrolysis reaction temperature took place between 500 and 800°C and waxes were collected and characterised for their fuel potential amongst their physical and rheological properties. The elemental carbon in the wax ranged between 81.04% to 87.67% showing high potential of carbon based material similar to the one of the original high density polyethylene (HDPE) feedstock material. Furthermore, the dynamic viscosity (at 40°C) ranged between 31 and 171 Centipoise. It is worth noting the that the fuel range of the wax was of high range of some 70% diesel fuel for material collected at 500°C which is attributed to the slow pyrolysis regime and the branched nature of the feedstock. This points towards utilising this product as a potential fuel source in addition to further upgrading instead of classical refinery ones.

Keywords: polyethylene, pyrolysis, diesel, energy, fuel.

1 INTRODUCTION

Thermal degradation in inert environments aimed at recovering value added products from plastics, has been classed at the top of the hierarchy of organic and plastic waste management technologies [1]. These technologies include pyrolysis whereby the material is treated in moderate to high temperatures (350–900°C) [2], in order to produce light non-condensable gases, oils, solid char and wax [3]. Various technologies and reactor set-ups are used to perform pyrolysis such as fluidised bed reactors (FBRs), conical spouted beds, fixed beds, screen reactors and rotary kilns [4]–[9]. Depending on the residence time and operating conditions, pyrolysis could also be performed in slow, flash or ultra-mode of operation [2], [10]. The primary product of the pyrolysis of polyolefin plastics is waxes formed as a result of the deterioration of the feedstock which for energy minimisation purposes to avoid further cracking, can be utilised as a standalone product specially in slow mode of operation [10]–[15]. Pyrolysis wax encompasses various advantages such as high embodied energy content and fuel range chemicals, ease of handling and storage; the use as a raw feedstock material in refining and petrochemical complexes for fuel production by cracking [13]–[15].

Due to the aforementioned reasons, attention to pyrolysis wax has been renewed nowadays as evidently so in R&D circles [14], [15]. This is also coupled with the fact that

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EU legislations have also started to influence the world over in managing plastic waste and diverting it from landfill sites [16]. The majority of plastic waste is comprised of polyolefins (62%) which has been accumulating around the world over due to the latest surge in demand associated with the COVID-19 pandemic [15], [17]. In this work, the pyrolysis of polyolefin plastic grade in the form of high-density polyethylene (HDPE) took place to produce waxes (pyro-wax) in a novel and patented fixed bed batch reactor. The pyrolysis reaction temperature took place between 500 and 800°C and waxes were collected and characterised for their fuel potential amongst their physical and rheological properties.

2 EXPERIMENTAL

HDPE was acquired as a virgin film extrusion grade (Equate Co.). The polymer was used as received in the form of pellets with a measured size of approx. 3 ×3 mm. The reported density, melt flow index and melting point as declared by manufacturer are 0.952 $g \cdot cm^{-3}$, 10 g/10 min and 131°C, respectively. The thermal profile of the feedstock is shown elsewhere [18]. The amount of 100 g of the virgin HDPE was subjected to thermal (non-catalytic) pyrolysis using a patented fixed bed reactor system with details shown previously in Al-Salem [6]. Wax yield was investigated between 500 and 800°C as an average of the three bed temperatures used in the operation. Slow pyrolysis was conducted and the wax collection was achieved post condensation (<3 h) without separating the heavy and light fractions using a heating rate of 5°C min^{-1} throughout.

The density of the wax produced was determined via specific gravity method as per the ISO 1183-1 namely using the immersion method-A. The wax sample was preheated to its pour point in a plastic cup and the density was calculated with respect to the specimen's apparent weight in air. Calorific Value (CV) was estimated following ISO 1928:20 by subjecting 0.5 g specimen to CAL3K Advanced bomb calorimeter under 3,000 kPa. The elemental analysis was also estimated for the wax samples. Duplicate 3 mg samples were subjected to a Perkin Elmer 2400 CHNS/O organic elemental analyser with an auto-sampler under reaction temperature varying between 925 and 1000°C depending on the element tested. The oxygen analysis of the instrument was calibrated using 1–3 mg of benzoic acid. Viscosity of waxes was determined using a cone and plate viscometer (HAAKE tester VTiQ) fitted with Peltier Temperature Controller. The dynamic viscosity value at 400 1 s^{-1} shear rate. Fuel range chemicals were identified using an Agilent 8,860 gas chromatography (GC) coupled with Agilent 5977B MSD mass spectrometer (MS) (HP5MS-UI Column, 30 m length, Stationary phase layer – 0.25 microns). Solid phase extraction was used for the processed analytes further on for characterisation.

3 RESULTS AND DISCUSSION

As mentioned in the first part of this communication, wax is the primary product evolved from the pyrolysis of polyolefin polymers namely polyethylene (PE). The devolitilisation that occurs in pyrolysis mechanism results in the residue that is called wax with a carbon range between C_{20} and C_{50} [17]. Wax is also responsible for adding to the gases and oils that accumulate as other pyrolysis products in the same mechanism [19]–[21]. Fig. 1 shows the yield of the wax formed and collected as an average of the duplicate experimental runs conducted in this work. With the exception of the 600°C experimental run, the yield was decreasing as a function of the reactor's temperature.

HDPE is a branched semi-crystalline polymer that is characterised as a lesser branched material than low density polyethylene (LDPE) and more so when compared to linear low-

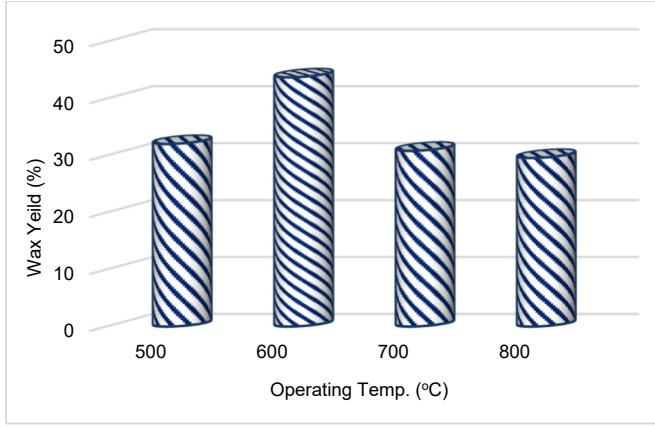

Figure 1: HDPE yields (wt.%) of wax with respect to reactor operating temperature.

density polyethylene (LLDPE). The cracking of wax was less evident when more heat (in the form of elevated temperature) at 500°C. This shows an estimated wax yield of some 32% (Fig. 1). Moderate synergy between the evolved gases and waxes was observed at 600°C to yield the highest wax (43%). Previous work conducted by other authors on PE using various set-ups show that wax yield reaches some 50% at 500°C with a gradual decrease [10], [22]. Fig. 2 shows the density of the wax obtained as a function of the reactor's temperature. A gradual decrease was observed in the analysed samples with an average density equal to 849.4 ± 5.32 kg·m^{-3}. The obtained density range is an agreement with previous reports on waxes and were higher than commercial wax (paraffin wax on the market) [23].

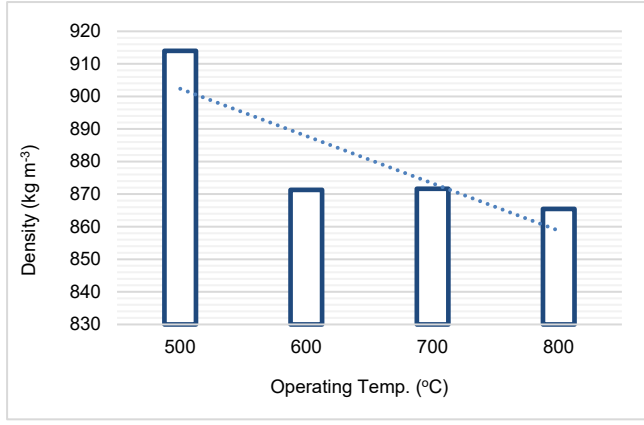

Figure 2: Density of wax (kg m^{-3}) with respect to reactor operating temperature.

The elemental analysis for the obtained wax as an average for all experimental runs was determined thus: Carbon (C, 79.46%), hydrogen (H, 17.77%) and sulphur (S, 2.77%). The calorific value (CV) was also estimated (average 46.22 kJ·g^{-1}) and is shown in Fig. 3.

There was no trend observed in the estimated values herein. It is quite important to highlight to aspects from the extracted work thus far. Firstly, commercial fuels have a CV range between 44.6 and 46.6 8 kJ·g^{-1} [24]. This shows that the wax in this work falls within said range promoting it as a potential fuel. Secondly, the wax has more than twenty-fold the S content that is permissible for diesel fuel engines fuels which also points towards the need for de-sulphurisation of the feedstock (wax) to obtain ultra-quality fuels using cracking. Fig. 4 shows the dynamic viscosity determined for the samples studied as a function of the reactor temperature. An incremental increase in a proportional manner was observed with the temperature. The range of the viscosity was between 31 and 171 centipoise falling in the range of waxy crude oil/asphaltene mix typically handled in refineries [25].

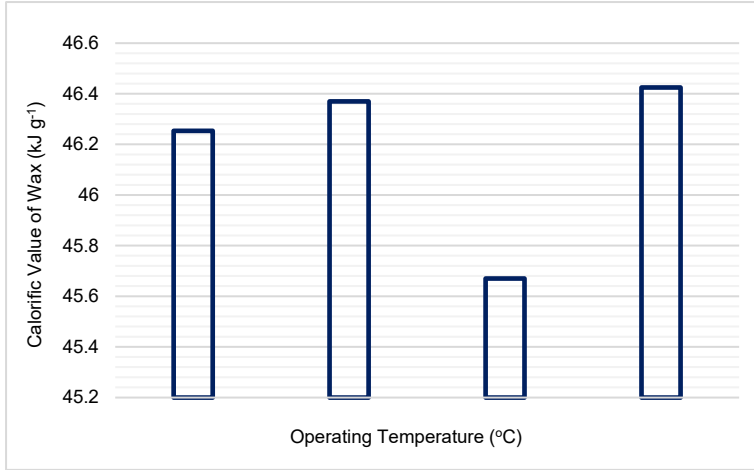

Figure 3: Calorific value of wax (kJ kg^{-1}) with respect to reactor operating temperature.

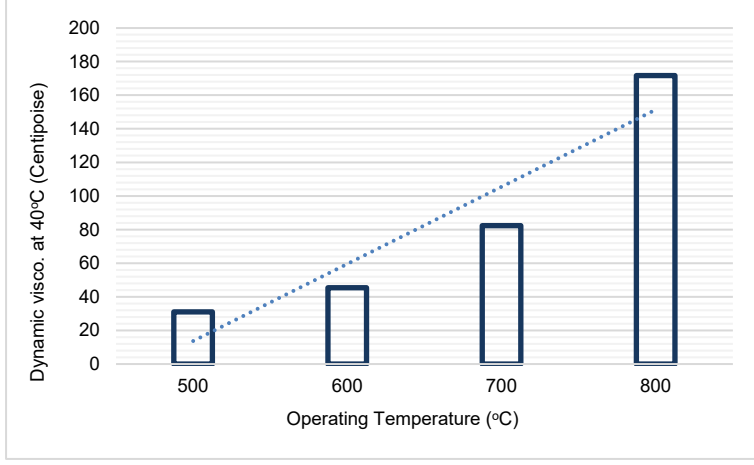

Figure 4: Dynamic viscosity of wax (centipoise) with respect to temperature.

Fig. 5 shows the chromatography of the studied samples by depicting the fuel range chemicals after characterising each carbon range as per the following: C_4–C_9 (petrol), C_{10}–C_{19} (diesel) and heavy waxes (C_{19}+). It is quite important to recognise the fact that the diesel fraction was increasing from about 15% at 500°C reaching 42.6% at 800°C. The concoction of the tested wax samples paves the way for future consideration of polyolefin waste that could substitute refinery feedstock for catalytic cracking. Fuel production could easily be achieved coupled with sulphur regulation that could reduce environmental impacts of plastic waste and dependence on crude oil sources of fuel.

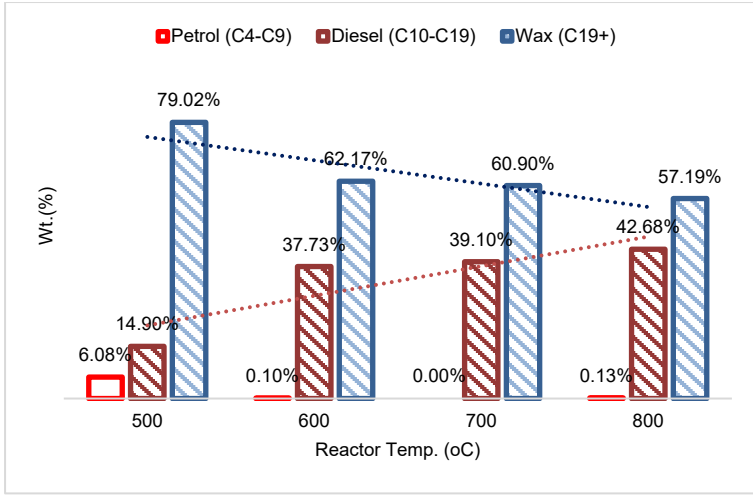

Figure 5: Chromatographic analysis showing fuel range chemicals detected for wax recovered from the pyrolysis of HDPE with respect to temperature.

4 CONCLUSIONS

In this work, high density polyethylene (HDPE) was subjected to thermal pyrolysis in the range from 500 and 800°C. The wax yield was at a maximum at 600°C reaching some 43% of the total reactor charge. The experimental characterisation of the samples showed that the wax conformed with fuels available on the market. Furthermore, the sulphur content exceeds the permissible limit of 0.1 wt.% which points towards the fact that de-sulphurisation is required to reduce the S element content. In addition, the diesel fraction in the samples reached some 42.6% for samples extracted at 800°C. In general, the fuel range chemicals show possibility of fuel production from the wax samples by cracking which makes it a suitable feedstock for refineries and petrochemical complexes. The work presented also provides a platform for circularity in the future where integration opportunities are possible with the oil and gas sector at one end; and environmental and waste management services at the other.

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