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Original scientific paper

EVALUATION OF DISTILLATION CURVE OF PYROLYTIC LIQUID FUEL

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A b s t r a c t: The natural catalyst, opalized silicate-tuff, was demonstrated to be an excellent catalyst for the breakdown of plastic waste and produced a high-yield liquid fraction. Polyethylene (PE) and polypropylene (PP) waste mixture has been catalytically degraded in a batch reactor operating in dynamic conditions, and the obtained liquid fuel is in the petrol and kerosene range. The yield of condensed product formation was higher than 85%. The ASTM distillation according to the requirements of the ASTM D86 Standard Test Method was performed. Under ambient pressure, the test method of determining the boiling range of a petroleum product by performing a simple batch distillation has been used. Some physical and qualitative characteristics of the condensed product were determined. The obtained condensed product, 65% is in the diesel range between 180°C and 320°C. The most common compounds in condensate are paraffin (78%) and aromatic (22%). The quantity of naphthenic is minor.

Key words: pyrolysis; ASTM distillation; natural catalyst; ASTM D86 Standard Test Method

ЕВАЛУАЦИЈА НА КРИВАТА НА ДЕСТИЛАЦИЈА НА ПИРОЛИТИЧКО ТЕЧНО ГОРИВО

А п с т р а к т: Природниот катализатор, опализиран силика-туф, се покажа како одличен катализатор за разградување на пластичен отпад и добивање висок принос на течно гориво. Отпадната смеса од полиетилен (PE) и полипропилен (PP) е каталитички разградена во шаржен реактор што работи во динамични услови, а добиеното течно гориво е во видот на бензин и керозин. Приносот на добиениот кондензиран производ е поголем од 85%. Извршена е ASTM дестилација според барањата на стандардниот тест-метод ASTM D86. Под амбиентален притисок, тест методот е користен за одредување на интервалот на вриење на нафтениот производ со спроведување едноставна шаржна дестилација. Утврдени се некои физички и квалитативни карактеристики на кондензираниот производ. Добиениот кондензиран производ е 65% во рангот на дизел помеѓу 180°C и 320°C. Најчести соединенија во кондензатот се парафини (78%) и аромати (22%). Количеството на нафтени е минорно.

Клучни зборови: пиролиза; ASTM дестилација; природен катализатор; стандарден тест-метод ASTM D86

1. INTRODUCTION

Petroleum is used excessively in modern civilizations as both a fuel and a raw resource for numerous businesses. Four percent is used to create plastic, four percent is used as feedstock for the petrochemical sector, five percent is utilized for other purposes, and about forty-five percent is used internationally to generate electricity [1]. Finding alternative energy sources to petroleum is therefore necessary. Recycling of waste plastics is a very important issue in order to relieve environmental pollution. Worldwide, the conversion of plastic waste to fuel by application of different pyrolysis methods has been intensively researched [2]. Particularly post-consumer plastics are a very attractive opportunity for utilization as a valuable and reusable source of hydrocarbons if they're broken down into lower molecular weight products [3]. Apart from energy concerns, the most promising substitute for plastics pyrolysis or recycling seems to be the development of more efficient techniques for transforming these inexpensive waste polymers in a way that is environmentally friendly [4].

During the cracking process of long polymer molecules, the degradation of polymer chains can be enhanced by applying various catalysts. The used catalysts have a high conversion effect over the plastic wastes at lower temperatures and decrease the activation energy [5]. The impact of zeolitic catalysts has been highlighted in polymer degradation catalytic processes that provide valuable hydrocarbons [6–9]. The effectiveness of non-zeolitic catalysts in the breakdown of polymers is far less understood. There have been reports on the catalytic conversion of plastic wastes using various non-zeolite catalysts. They consist of the following: alumina, silica, and basic catalysts like $BaCO_3$ [10], bimetallic catalysts, Al-Zn composites [11], FCC catalysts [12, 13], and mesoporous catalysts like Al-MCM-41 [14]. Hydrocarbons are produced during catalytic degradation, which occurs at temperatures that are comparatively low and within the motor fuel range [15, 16]. Liquid fuel is probably the most valuable in such a degrading process. Natural opalized silicate–tuff proved to be an excellent catalyst for plastic waste degradation and producing a high yield liquid fraction with gasoline and kerosene [17].

The liquid fuel obtained from catalytic pyrolysis could be used as a transport fuel because of the high amount of aromatic and some naphthenic compounds that could be a good motor fuel since. Aromatic and naphthenic compounds improve the quality of gasoline by increasing the octane number [18]. Olefinic compounds are industrially more attractive than even the pure saturated compounds [19], as they are intermediaries of many valuable and expensive chemicals.

Distillation is a primary process widely used in the oil and petrochemical industries, providing important qualitative and quantitative information on complex fuel mixtures [20]. The ASTM D86 distillation process is presented with a curve that plots the liquid mixture's boiling temperature against the total volume of distillate at a specific pressure [21]. This standard of the American Society for Testing and Materials (ASTM) covers distillation characterization techniques, describing a basic distillation procedure [22].

In this work, the efficiency of these natural catalysts for the production of liquid fuel from waste plastic was analyzed. The obtained condensed fraction obtained from catalytic degradation of polyethylene (PE) and polypropylene (PP) is much larger than the gaseous fraction. The physical properties of obtained liquid fuel were determinate. The pyrolytic fuel was analyzed according the ASTM D86 standard. The main constituents of pyrolytic oil, paraffin's, naphthenic, and aromatics, were determined using the n-d-M method.

2. EXPERIMENTAL

2.1. *Materials*

The waste polymer mixture used in this work was consisted of 76.2% high-density and 23.8% polypropylene. The natural alumina-silicate catalyst tuff was screening through the sieve, and the fraction of 0.03 mm was employed in the experiments. The catalyst activation was performed at 800°C for 3 h.

2.2 *Experimental setup*

A stainless steel 400 ml batch reactor was used for the production of liquid fuel in the presence of tuff catalysts. The PID (Unitronics V570) controller controlled the temperature and maintained a constant heating rate of 10°C/min.

The full procedure for the production of liquid fuel was presented in our previous work [23].

The obtained pyrolytic oil was evaluated using ASTM distillation, according to the requirements of the ASTM D86 Standard Test Method, in the apparatus depicted in Figure 1. A basic test method of determining the boiling range of a petroleum product by performing a simple batch distillation has been used. The yield of condensate product and temperature are systematically measured. Additionally, are noted the residual volume. The ASTM D86 test method determines quantitatively the boiling range characteristics of products as light and middle distillates. Also, standard assays are used for fuel quality control, and results rely on several fuel characteristics, such as specific gravity and distillation curve. These attributes are closely linked to the composition of the fuel, and predicting them requires understanding the features of its constituent parts.

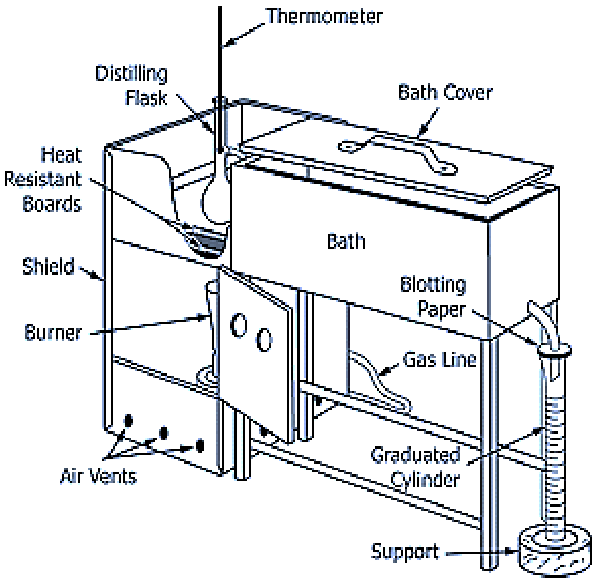

Fig. 1. ASTM distillation apparatus according ASTM D86 test method [20]

3. RESULTS AND DISCUSSION

The experimental measurements are made on each 5 vol% of distillates. In calculations of characteristics of pyrolysis fractions, the essential boiling points of 10, 30, 50, 70, and 90 vol%, were used. The distillation (volatility) characteristics of hydrocarbons have an important effect on their safety and performance. Understanding the volatility of complex fluids, and particularly the behavior of fuels in a refinery or engine, depends on their characteristics. Plotting a liquid mixture's boiling temperature against its distilled volume percentage is the ASTM distillation curve method (Figure 2). The distillation curve relies on the type and quantity of compounds present in the mixture. The volumes of the lighter phase of the pyrolytic fuel with a boiling point below 175ºC is the fraction that corresponds to the gasoline range (220ºC), and are only 35% of the total collected sum of all fractions. Consequently, a greater amount, 65% of condensate, is obtained in the diesel range between 175°C and 320°C. Distillation ended at 316ºC and 90% volume.

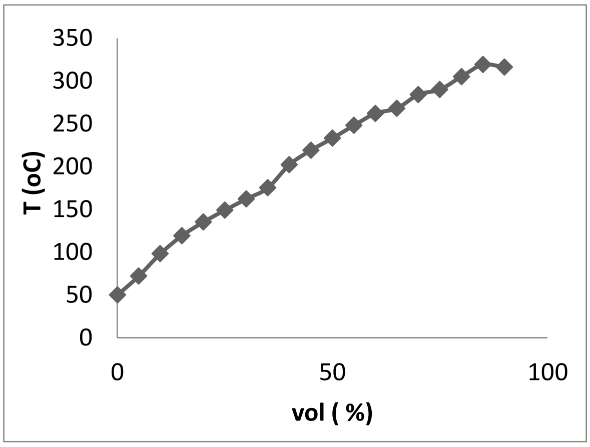

Fig. 2. ASTM distillation curve

The distillation characteristics of fuel are critically important. The presence of high boiling point components in these and other fuels can significantly affect the degree of formation of solid combustion deposits.

The determination of the chemical properties of pyrolytic fuel is usually complex and expensive due to the large number of different compounds. Physical properties such as density, kinematic viscosity and refractive indexes were determined by measurable laboratory tests, according to specific standards. The fundamental variables for calculating correlations that meet the standard test method are the density and distillation curve. The density and kinematic viscosity were determined according to ASTM D4052 and ASTM D445 and D446, consequently. Refractive index follows ASTM D1218 and aniline point ASTM D611 (Table 1).

Table 1

Measured physical properties of obtained liquid fuel

Physical properties	Labels	Units	Measured values
Density	d	g/cm^3	0.7801(15ºC) 0.7764 (20ºC)
Refractive index	RI	–	1.4410 (25ºC)
Kinematic viscosity	V	cSt	0.9765 (40ºC)
Aniline point	AP	ºC	66.3

The values shown below are computed using the distillation data according the ASTM D86:

API – American Petroleum Institute gravity

SG – Specific gravity

VABP – Volumetric of average boiling point temperature (ºC)

S^{ASTM} – The slope of ASTM curve (ºC/vol%)

MeABP – Mean average boiling point (ºC)

MABP – Molar average boiling point (ºC)

CABP – Cubic average boiling point (ºC)

νsus (SUS) – Kinematic viscosity to Saybolt Universal seconds

MW – Molecular weight (g/mol)

Kw – Watson characterization factor

These properties rely on the volumetric and volatility characteristics of the mixture, which, in principle, can be obtained by the use of a thermodynamic model and the chemical composition of the mixture.

It is possible to predict the parameters for pyrolytic oil characterization based on the results shown in Table 2, including molecular weight (MW), volumetric average boiling point (VABP), mean average boiling point (MeABP), and the value of Kw. Therefore, lower values of VABP and MeABP, 213 and 218, as well as MW 138, suggest lighter fuel, whereas higher values are expected for heavier fuels. Therefore, a MW ranges from 70 to 200 for lighter fractions and between 200 and 600 for heavier fractions. This is even more confirmed with the value of the Kw factor, which comprises a classification method according to the variety of paraffinic, naphthenic, intermediate, or aromatic in the pyrolytic oil. Typical ranges of Kw are between 10 and 13. The obtained value for the Kw factor of 11.9 ~ 12 implies a hydrocarbon compound predominantly paraffin in nature. Hydrocarbons with higher naphthenic or aromatic content are indicated by lower values of this factor. Values of 10.0 or less are seen in highly aromatic hydrocarbons. The boiling range gives information on the composition (Table 3), the properties, and the behavior of the fuel during storage and use.

Table 2

Calculated values using n-d-M correlation

SG	0.78
VABP	218.6
CABP	208.6
S^{ASTM}	3.1
MeABP	213.6
MABP	172.6
Kw	11.9075
νsus	1.02
MW	138.18

Table 3

Calculated % of groups of compounds using n-d-M

C_A	18.660
C_N	3.14
C_P	78.20

C_A – Aromatic ring structure (%)
C_N – Naphthenic ring structure (%)
C_P – Paraffin chains (%)

The volatility properties of gasoline are closely related to its performance within the engine; particularly, the adequate balance between light and heavy hydrocarbons is a determinant for engine cold start, engine heating, and fuel economy at cruising speed. If excess light hydrocarbons are present in gasoline, problems such as vapors lock and engine freezing may occur [24].

4. CONCLUSION

In this work, the ASTM D86 Standard Test Method was used for characterization obtained pyrolytic fuel over employed catalys – opalized silica tuff. This test method covers the atmospheric distillation of petroleum products and liquid fuels using a laboratory batch distillation unit to determine quantitatively the boiling range characteristics of such products as light and middle distillates. A characterization of the obtained pyrolytic fuel was made using the data obtained from ASTM distillation curve. The results obtained from the distillation curves indicate that pyrolytic fuel is a complex mixture of compounds.

The obtained pyrolytic oil was quantitative and qualitatively characterized. The fraction that corresponds to the gasoline range (175ºC) is only 35%, and a greater amount, 65% of condensate is obtained in the diesel range between 175°C and 316°C. The most common compounds in oil are paraffin's 78% and aromatics 22%. The quantity of naphthenic is minor, only 3%.

The molecular weight of fuel is 138, and the two estimated boiling points (VABP and MeABP) values of 213 and 218 suggest lighter fuel. As well as obtained value Kw of 12 implies a fuel with paraffinic nature.

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