Chemistry Research Journal, 2020, 5(4):219-225

Available online www.chemrj.org

Research Article

ISSN: 2455-8990
CODEN(USA): CRJHA5

Fuel from Used Motor-Oil by Visbreaking Process

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Abstract The purpose of this study is to obtain fuel products such as gases, aromatics-rich gasoline, gas oil and residuals by visbreaking of used motors-oil sample with desired adequate standard quality. The properties of raw used motors-oil sample were determined. In this research, we noticed that temperature, pressure and residence time have played an important role in determining the yields and the properties of the products. The optimum conditions were determined, at a temperature (t) 445 °C, an absolute pressure (P) 3.4 bar, and residence time (τ) 209 sec. The highest yields of produced cuts especially gasoline and gas oil, have also been obtained and respectively reached the average of optimum conditions to 19.8 wt. % and 27.6 wt.%. Produced gases are of high value and are mainly composed of methane, ethylene, and acetylene in addition to some proportions of normal and iso propane and butane. The yield was about 20 wt.%. The obtained gasoline cut contains 0.19 wt.% of Sulfur and a large proportion of aromatic compounds. The yield of gasoline sample was about 27 wt.%, and mainly contains single ring of aromatic compounds such as benzene, toluene, xylenes, as well as a large proportion of olefinic products. However, the produced gasoline and gas oil are unstable and of low-quality. Three liquid cuts are obtained: gasoline, gas oil and residuals by applying the visbreaking process method for the recovered used motor-oil sample.

Keywords Fuel, Used lubricating oil, Visbreaking, Mild thermal cracking, Gas oil, Benzene

Introduction

Lubricating oils had been degraded by use, losing their operational properties, and had become unable to function to the fullest. Moreover, their specification changes slowly to lower quality after being used in engines, equipments and machinery due to oxidation process as a result of heat, friction, impurities, water and due to the decomposition of additive compounds which are essential to improve the quality of lubricating oils. Therefore, they are usually replaced by new ones [1,2]. Used oil is a source of pollution to the surrounding. For example, in some cases it is thrown in holes in the ground and then diffuses to water basin, or it is thrown in rivers and water sources, or used as direct fuel in boilers. Regenerated used oil by known chemical methods like acid treatments or adsorption, extraction or by mixed methods leading to lower quality oil [3,4,5].

Lubricating oils are complex compounds that contain (20-60) carbon atoms, of molecular weight (300 –750 Kg/Kmol), and boiling points (300–650°C). They are composed of linear and iso-paraffin's, naphthenic hydrocarbons having 5-6 rings in paraffinic chains, aromatic compounds with single and poly rings, and aromatic-naphthenic rings having side paraffinic chains, in addition to the additives compounds [6,7,8].

In recent years and after the surge in petroleum prices and its products, energy resources have become fundamental requirements to be secured, and this has prompted interest in the logical use of the used oils since they are rich sources in valuable hydrocarbons [5,8].

With the increasing industrial progress and population growth in Syria, the demand for petroleum products has increased, especially diesel and benzene fuel, at a time when approximately 60% of the national need is imported. Hence, the idea of this research is to get benefit from the hydrocarbons existing in used oils and to transform them into useful products via preliminary treatments of used oil followed by either visbreaking or catalytic transformation. This aims at obtaining useful products of higher economical values [7,9,10].

Materials and Methods

In these studies, **a** sufficient quantity of different types of used motor-oil was collected directly from gasoline, diesel and hydraulic motor-oil service stations. The collected used motor-oil sample was mixed very well and was primarily treated according to the following steps:

-Settling to allow the separation of a small amount of water and heavy material deposited at the bottom of the bowl assembly.

-Dewatering and light fuel evaporation (atmospheric distillation) by heating the oil sample up to 200 ^{o}C and thus freeing it of water and light fuel. This sample was considered a raw sample and its characteristics were determined and shown in table (1). This operation makes it easier to treat the sample in subsequent proceedings.

-Distillation of the raw used-oil sample under low pressure (vacuum distillation, 10 mmHg) using an automatic vacuum distillation unit. About 80 wt.% of the raw used-oil sample was recovered. This sample was used in subsequent experiments.

The volumetric and gravimetric yields and properties of raw, recovered and residual samples of used motor-oil are shown in Tables (2,3,4) and figure (1).

In another set of experiments, the recovered used oil sample is used in the visbreaking process in order to obtain useful fuel products. The Box-hunter methods (MINI TAB Project) were used to determine the necessary minimum number of experiments and to define the ranges of parameters that can be experimented [11]. This is done by solving the necessary equations and calculating the important figures to define the optimum conditions for each set of experiments and to establish the correlations between the experimental conditions and properties of the main products. Correspondence between calculated and experimental values was found. Programmed experiments were used in order to study the effects of the main influencing factors within the chosen following ranges of temperature: (430–480°C), total nitrogen pressure: (1-6 bar), and gas flow: (200 – 400) ml / hr.

So many experiments have been carried out to determine the optimum condition for the visbreaking process of the recovered used oil sample. A steel automated pilot plant unit was used in order to realize the planned experiments under defined conditions. The unit was initially flushed by nitrogen gas, pressurized and controlled to constant required nitrogen pressure values during all subsequent experiments. The other operating conditions were controlled, then the visbreaking process took place and some coaks were formed and observed. Thus, the conditions were chosen to minimize the coaks formation. Gas and liquid products were collected and analyzed according to the standard methods [12], including gas chromatography and GC- mass techniques.

In many experiments, gas yields at optimum conditions were about 20 wt.%, and their average composition was: CH_4(30-50%). C_2H_4(11-19%), C_2H_6(15-35%), C_3H_6(7-12%), C_3H_8(6-15%), i-C_4(0.3-1.4), n-C_4(2-9), i-C_5(~0.5), n-C_5(~0.5), H_2S(~0.1 %), CO_2(2-6%), H_2(1-2 %).

A weighed amount of the produced liquid sample for each experiment was taken and then distilled according to the ASTM D 86 method and was also separated to three main cuts : gasoline (C_5 - 165°C), gas oil (165 – 350°C), and residuals (+350 °C). The resulted three main cuts were weighed and the yield, the total degree of transformation, and the liquid degree of transformation were calculated for the visbreaking process. A summary of the results is shown in table (5).

Results and Discussion

The purpose of this research is to obtain useful products such as gasoline and gas oil from used motor-oil with desired adequate standard quality. The main properties of the purified recovered used oil sample are clarified in table (3), which shows that Conradson carbon number has dropped (0.04 wt.%) because the sample is free of water and light fuel, in addition to a low content of metals especially sodium (0.49 ppm). This enables the sample to be used in subsequent treatments like visbreaking or catalytic hydro-cracking. The properties of residuals resulting from the cut (+565 °C) are shown in table (4). However, residuals still contain a significant proportion of the oil. Nevertheless, they can't be used as a fuel for boilers due to environmental restrictions (because of their high content of metals especially lead 272 ppm).

The initial flow sheet for the treatments of the used motor-oil sample is shown in figure (2), which sums up the steps of treatments, the yields of products obtained, and some of their properties.

The operational conditions used in this process are mild and lower than those usually used in viscosity reducing of feedstock. This is because the specific weight of the recovered used oil sample is less than the usual used raw materials. Moreover, the tested oil sample is free of asphaltic compounds. Therefore, there is no need for severe operating conditions.

The best features possible within the operational ranges that have been working out are:

-Temperature is low and falls within the domain (443-447 °C).

-Pressure values at the middle and is located within the domain (3.3 - 3.5 bar).

-Residence time in the reactor is located within the domain (196-221 sec).

So the average best values of those operating conditions were 445°C, 3.4 bar and 209 sec and represents the optimum conditions. Sample properties, the optimum operating conditions, product yields and their properties are summarized in table (5), and figure (3). Despite the low severity of the process, the optimum conditions obtained led us to the highest yield of gasoline (20 - 21 wt%) and a higher yield of gas oil (25 - 28 wt%).

By examining the results obtained and shown in tables (2,3,5), we can notice that the amounts of gas output, and the loss in liquid were high in most experiments, due to the carbonization process and coaks' deposition inside the reactor. This, in turn, means that the products of cracking compounds are unstable. This has been clear due to the yellow to brownish color of the gasoline and of gas oil, which indicates the presence of high content of unsaturated compounds (aromatics and olefins). By increasing the temperature, the loss of liquid would rise and the amount of gases would increase subsequently. If the pressure was increased, the coaks and gases formation would be less, but the formation of olefinic compounds would be enhanced. Residence time has also played an important role and increasing the residence time would allow a sufficient time for deep transformation, the reactions of polymerization and condensation would take place, and the liquid yield would be less. However, gas yields would be high, and the composition of all liquid products would be affected in favor of aromatics and olefins formation. Thus, an adequate residence time is necessary.

Produced gases are mainly composed of methane, ethylene, and acetylene in addition to some proportions of normal and iso propane and butane. The gases can be a source of high value compounds and can be separated into desired petrochemical species or used as direct fuel. Obtained gasoline contains a large proportion of aromatic compounds which have a single ring and have reached its maximum in some experiments. By determining chemical compound groups based on the results of chromatographic analysis by GC- Mass technique, we have found (benzene 5.64 wt. %, toluene 9.35 wt.%, xylenes 9.55 wt.%), as well as a large proportion of olefinic compounds. The gasoline produced is of low-quality due to the high content of sulfur (0.19-0.22 wt%) and olefins. The produced gasoline can be a source of those types of aromatics and unsaturated compounds which are desirable in many petro-chemical applications and industries. Produced gas oil is also of a standard quality except for its content of sulfur which is higher than the raw material (0.55-0.70 wt.%). It needs to be treated by hydrogenation of unsaturated compounds and desulfurization operation. It is better to treat the recovered used oil sample by hydrocracking or catalytic cracking in order to minimize the liquid mass loss and to improve the quality of the products.

Table 1: Main properties of the used motor oils (raw sample)

Property	value	Test Method
Sp. Gr. (d_4^{15})	*0.8933*	*ASTM D 4052*
Conradson carbon, wt.%	*2.1943*	*ASTM D 189*
Water Content, Vol.%	*0.8*	*ASTM D1796*
Ash Content, wt.%	*1.485*	*ASTM D 874*
Sulfur content, wt.%	*0.60*	*ASTM D 4294*
Viscosity at mPa	*107.57*	*ASTM D 5133*
40°C cSt.	*122.64*	-
Flash Point (Open Cup), °C	*196*	*ASTM D 92*
Fire Point (Open Cup), °C	*248*	*ASTM D 92*
Pour Point, °C	*- 19*	*ASTM D 5985*
Metals Content, ppm	*ASTM D 4628*	

Na	*Ni*	*Pb*	*Fe*	*Cu*	*Zn*	*Cd*
1.18	*0.99*	*51.14*	*20.21*	*8.95*	*51.04*	*0.38*

Table 2: Results of volumetric and gravimetric yields of used motor oils (Raw, Recovered and Residual Samples).

Substance		Weight, gr	Wt. %	Vol. ml	vol. %
Used motor oils		*180.805*	*100*	*202.4*	*100*
water	(200°C)	*1.685*	*0.93*	*1.65*	*0.62*
Light fuel		*0.637*	*0.35*	*0.75*	*0.32*
Vacuum distillation cut (recovered)		*178.483*	*98.72*	*200.0*	*99.06*
(200 – 263°C) Light fuel		*0.646*	*0.36*	*0.75*	*0.09*
(263 – 565°C) Recovered used oil sample		*144.303*	*79.81*	*163.7*	*81.04*
Vacuum distillation residual (+565°C)		*33.534*	*18.55*	*35.55*	*17.93*

Table 3: Properties of a recovered used oil sample

Property	Value	Test Method
Sp. Gr. d_4^{15}	0.8815	ASTM D 4052
Sp. Gr. d_{15}^{15}	0.8823	ASTM D 4052
Conradson carbon, % wt	0.04	ASTM D 189
Sulfur content, % wt	0.52	ASTM D 4294
Viscosity at 40°C, cSt	48.08	ASTM D 445
Viscosity at 100°C, cSt	6.978	ASTM D 445
Viscosity Index	101	ASTM D 2270
Color	6.0	ASTM D 1500
Flash Point (Open Cup), °C	204	ASTM D 92
Fire Point (Open Cup), °C	240	ASTM D 92
Cloud Point, °C	-5	ASTM D 2500
Pour Point, °C	-6	ASTM D 5985
C_5 Insoluble's, % wt.	< 0.01	ASTM D 4055
Ash Content, % wt	< 0.005	ASTM D 874
API	28.88	
Mw, Kg l Kmol	480	(a)
High Heating value, Kj/Kg	46250	(b)
Net Heating Value, Kj/Kg	43050	• & (b) calculated

Table 4: Properties of residual vacuum distillation

Property	Value	Test Method
d_4^{15}	*0.9433*	*ASTM D 4052*
API	*18.37*	*ASTM D 4052*
$d_{50°C}$, *Kg* /m^3	*922.9*	*ASTM D 4052*
Sulfur, % wt	*0.977*	*ASTM D 4294*
Conradson carbon, % wt	*12*	*ASTM D 189*
Viscosity at 50°C, mPa.s	*320.8*	*ASTM D 5133*
Viscosity at 50°C, cSt	*347.6*	*calculated*
Flash Point (Open Cup), °C	*298*	*ASTM D 92*
Fire Point (Open Cup), °C	*352*	*ASTM D 92*
Ash Content, % wt	*7.915*	*ASTM D 874*

Metals Content, ppm						***ASTM D 4628***
Na	*Ni*	*Pb*	*Fe*	*Cu*	*Zn*	*Cd*
4.20	*4.60*	*272*	*107*	*47.6*	*269.7*	*1.81*

Table 5: Details of the Visbreaking process of recovered used motor oils, optimum conditions, products' yields, composition and properties

parameters	Optimum operating conditions		Products		
	range	Average		range	Average
Temperature, (°C)	443 – 447	445	Gases:	18.2 – 22.7	20.4
Pressure, (bar)	3.3 – 3.5	3.4	Gasoline, (C_5 – 165°C)	18.8 – 20.7	19.8
Residence time, (sec)	196 – 221	209	Gas oil, (165 – 350°C)	26.8 – 28.4	27.6
Total conversion, wt. %	67.0 – 74.0	70.5	Residue, (+350 °C)	30.7 – 32.3	31.6
Liquid conversion, wt.%	59.8 – 63.4	61.6	Coaks	0.5 – 0.9	0.7
			Total	**100**	

Products	Sulfur wt.%	Sp. gr.	Saturates Wt.%	Olefins wt.%	Aromatics wt.%
Gasoline, (C_5 – 165°C)	**0.730**	**0.190**	**15.83**	**57.05**	**27.12**

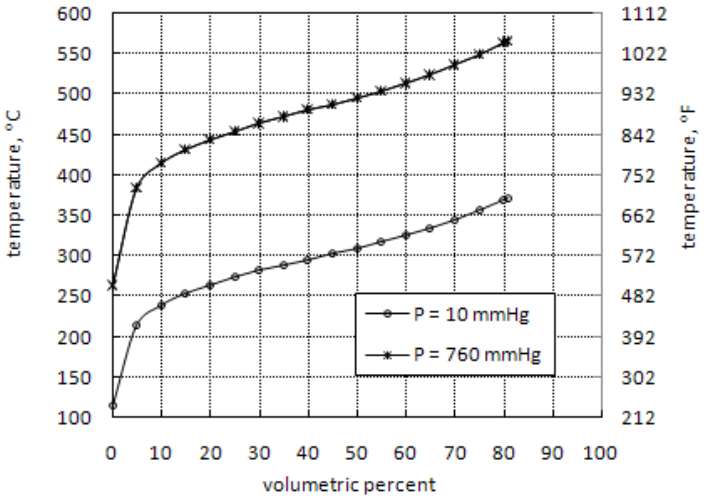

Figure 1: ASTM Distillation curve for a primary treated used motor Oil sample

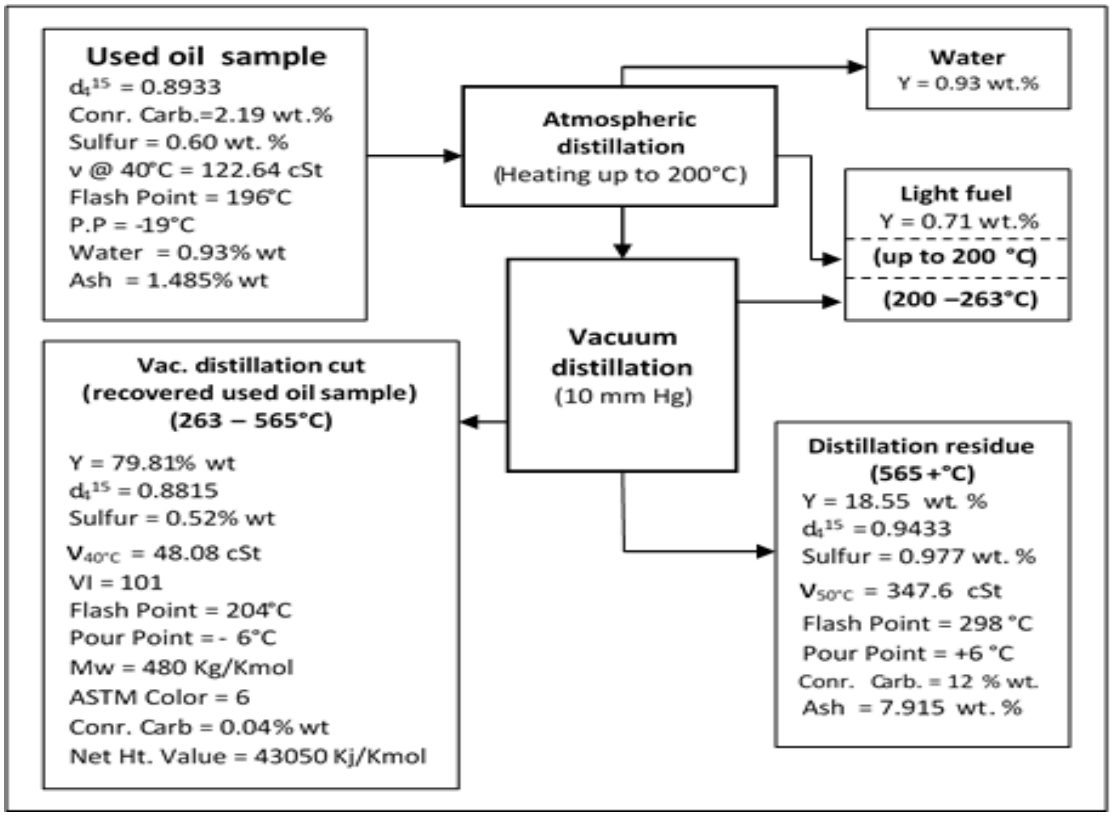

Figure 2: Initial flow sheet for primary treated used motor oils (products & properties)

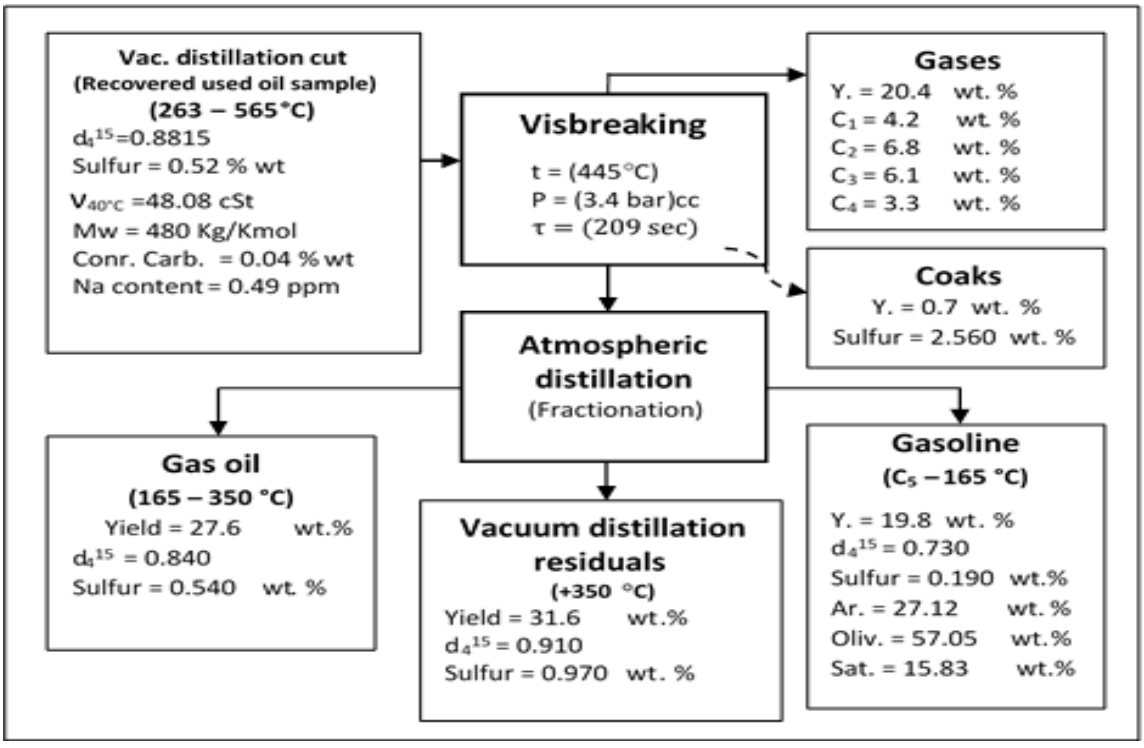

Figure 3: Initial flow sheet of visbreaking results of a recovered used oil sample

Conclusions

By applying the visbreaking process method for the recovered used motor-oil sample and as a conclusion of many performed experiments, we have found out the following:

-Produced gases are mainly composed of normal and iso (C_1-C_4), and their yield was high and was achieved in an average of 20.4 wt.%. This indicates that the mass losses were also high due to carbonization reactions, and could be used as a source of desired petrochemical compounds or as a fuel.

-Three liquid cuts are obtained: gasoline (C_5-165°C), gas oil (165-350°C), residuals (+350°C), and their yields are (19.8 wt.% For gasoline; 27.6 wt.% for gas oil; 32.2 wt.% for residuals).

-The obtained gasoline contains high content of aromatic compounds which have single rings. It has reached up to (5.64 wt.% Benzene, 9.35 wt.% toluene, 9.55 wt. % xylenes) in the optimum conditions experiment. The produced gasoline is of low-quality due to its high content of sulfur (0.190 wt.%) and high content of olefinic compounds (57 wt. %), so it must be hydro-treated before it can be incorporated into a finished product. However, produced gasoline can be a source of aromatics and unsaturated compounds which are desired in many petrochemical applications and industries.

-Produced gas oil is of a good quality, except for its content of sulfur which is higher than the raw material (0.540 wt.%). It needs to be hydro-treated by catalytic hydrogenation in order to eliminate unsaturated and sulfur compounds.

Compliance with Ethical Standards

This study was not funded by any institution. It is a product of our working team and was carried out in our laboratory at Al-Sham Private University (ASPU), the faculty of engineering-department of chemistry.

This is an authenticated original research paper, never been submitted for publication in any other journal, nor been transferred or copied from other relavent sources.

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