Treatment of Slack Wax by Thermal Cracking Process

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Abstract

This work deals with thermal cracking of slack wax produced as a byproduct from solvent dewaxing process of medium lubricating oil fraction in AL-Dura refinery. The thermal cracking process was carried out at a temperature ranges 480-540 ℃ and atmospheric pressure. The liquid hourly space velocity (LHSV) for thermal cracking was varied between 1.0-2.5 hr^{-1} . It was found that the conversion increased (61 - 83) with the increasing of reaction temperature (480 - 540) and decreased (83 - 63) with the increasing of liquid hourly space velocity (1.0 - 2.5).

The maximum gasoline yield obtained by thermal cracking process (48.52 wt. % of feed) was obtained at 500 ℃ and liquid hour space velocity $1.0\,hr^{-1}$. The obtaining liquid product at the best operating condition 500 ℃ and LHSV $1.0\,hr^{-1}$ was fractionated into wide range fractions. Based on the determination of some properties for the distilled fractions and comparison (these properties with that required by standard requirements) it is possible to use the fractions of cracking products as a component for production of automobile gasoline, domestic kerosene, light diesel fuel and basic lubricating oils.

Keywords: cracking slack wax.

Introduction

The petroleum wax is the byproduct of a dewaxing process of lubricating oil fractions; the de waxing operation removed relatively small proportion of wax components from a large proportion of oil to produce slack wax, generally brown in color and has oil content between 5-25%.

The commercial slack wax contains 79-89 wt. %. of paraffins and has a melting point in the range of 48-55 ℃ and flash point of about 150 ℃ [1, 2]. The slack waxes are also reported to contain (0.5-0.7) % wt. of sulfur and to have traces of water [3, 4].

Thermal cracking reactions are those that occur in the temperature range of (460-540 ℃) to a point at which the bonds that hold a molecule together are broken. This breaking of bonds results predominantly in an increase in smaller molecules. However, breaking of bonds also leads to free radical formation, which can also result in subsequent polymerization or condensation reactions [5, 6]. Cracking reaction starts to occur at a temperatures of about 315-370 ℃ depending on the hydrocarbon nature of the material being cracked.

Depending on feed stock type and product requirement thermal cracking

can be carried out over a wide range of temperature from 450-750 ºC and at pressure varying from atmospheric to 70 bars [7].

The objective of the present work is to study the thermal cracking processes of slack wax at different operating conditions in continuous laboratory unit.

Experimental Work

1. Feed stock

Slack wax obtained from the solvent dewaxing process from AL-DURAH REFINARY was used as a feed stock in this investigation. The properties of slack wax are shown in Table 1.

Table 1: Slack wax properties

Characteristics	Value
Viscosity, Cst. At 40 ºC	13.8
Specific Gravity, at 15.6 ºC/15.6 ºC	0.804
Pour point, ºC	48
Color	Dark
Neutralization number, mg. KOH/g. oil	0.075
Melting point, ºC	76
Oil content, % wt.	20

2. The experimental procedure

The thermal cracking experiments were carried on a laboratory continuous flow unit shown in Fig. 1. The desired quantity of molten feed slack wax was pumped from the feed storage by a dosing pump to the preheater and then the preheated feed entered the reactor section. The reactor consisted of a stainless steel tube with 3.0 cm inside diameter and 60 cm length. The reactor was heated and controlled automatically by three heaters insulated by two layers of insulation to minimize heat losses. The temperatures inside the reactor were measured by three thermocouples fixed inside the reactor at three different locations.

The vapor and liquid products were discharged to the condenser and the condensates were collected alone, for all runs in various operating conditions. The uncondensed gases were collected in gas collector unit. The duration of the time for all experiments was kept at 30 minute. The experiments took place at temperatures 480, 500, 520 and 540 ºC and liquid hour space velocities 1.0, 1.5, 2.0 and 2.5 hr^{-1}.
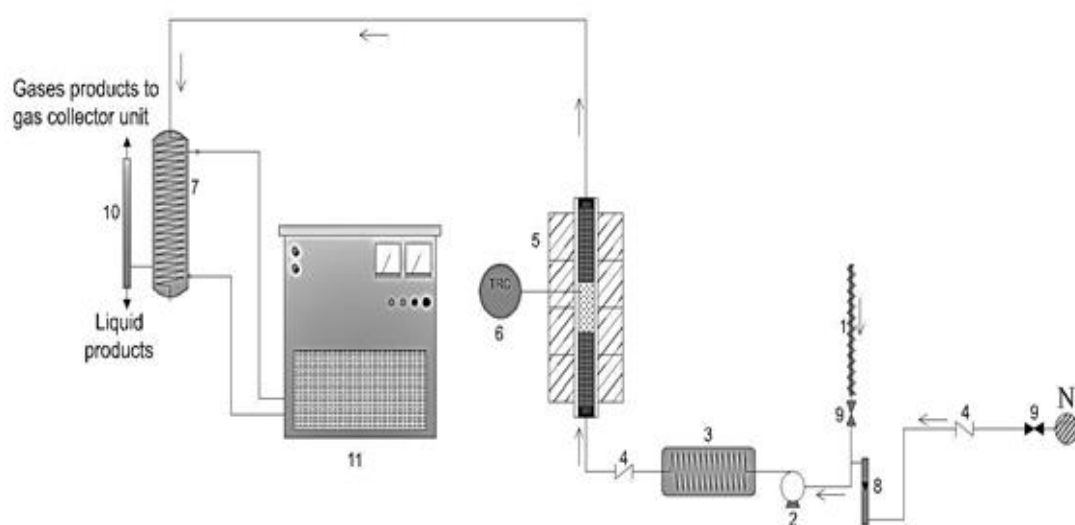
1-Feed reservoir: 2- Dosing pump; 3-Preheater; 4- One way valve; 5- Reactor system; 6- Temperature controller; 7- Condenser; 8- Flow meter; 9- Control valves; 10- Separator; 11- Cooling machine.

Fig. 1: Schematic flow diagram of laboratory continuous cracking unit

Liquid Product Distillation

1. General Distillation

  The general distillation of cracking liquid products was done according to ASTM D86 for separation fractions up to 220 ℃ called gasoline while the residue above 220℃ was called light cycle oil (LCO).

2. Wide Range Fractionation

  Distillation of thermal cracking liquid products into wide range fractions was achieved in Micro TOP-P distillation unit according to ASTM D-5236. The atmospheric distillation was continued until the temperature of column flask reached 350 ℃ and then the vacuum distillation at 60 mm Hg. was carried on until the top temperature of column reached 375 ℃ (520 ℃ at 760 mm Hg.). During the wide range fractions for thermal cracking products, the following fractions were separated : light naphtha (up to 75℃), heavy naphtha (75-175 ℃), kerosene (175-225 ℃), gasoil (225-390℃), light lubricating oil (390-430 ℃), medium lubricating oil (430-450 ℃) and heavy lubricating oil (450-520 ℃) according to 760 mm Hg., or (260-280 ℃), (280-320 ℃), (320-375 ℃) according to 60 mm Hg.

Results and Discussion
The Effect of Operating Conditions

  The effect of liquid hour space velocity (LHSV) in the range 1.0-2.5 $hr.^{-1}$ on slack wax conversion and the yield of gases, gasoline, light cycle oil and coke were studied at temperature ranges of 480-540 ℃. Fig. 2 shows the effect of LHSV on the slack wax conversion at different temperatures. As shown in this figure, the slack wax conversion increases with decreasing of LHSV at constant temperature. This means that the conversion of slack wax is a function of reaction time, the increasing of the contact time of the feed molecules increases the slack wax conversion and inversely proportional to the feed flow rate [8]. The decreasing LHSV at constant temperature increases the yield of gases, gasoline, coke, and decreases the light cycle oil.

Clear pictures for cracking products distribution at different LHSV and constant temperatures were presented in Figures 3→6.
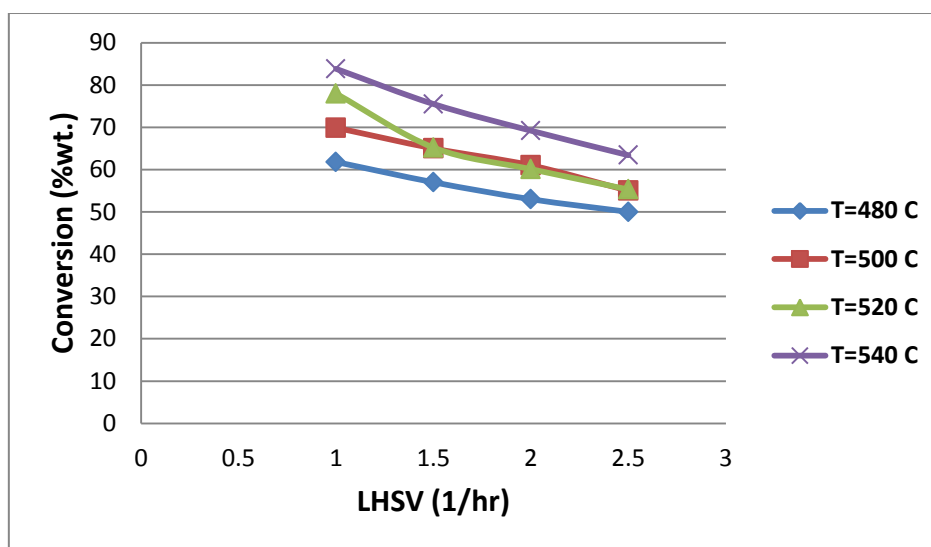

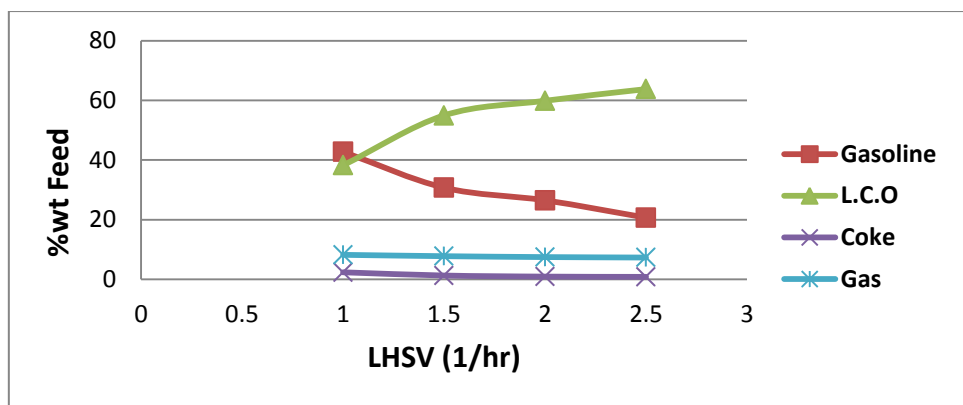Fig. 2: Effect of LHSV on the slack wax conversion at different temperatures

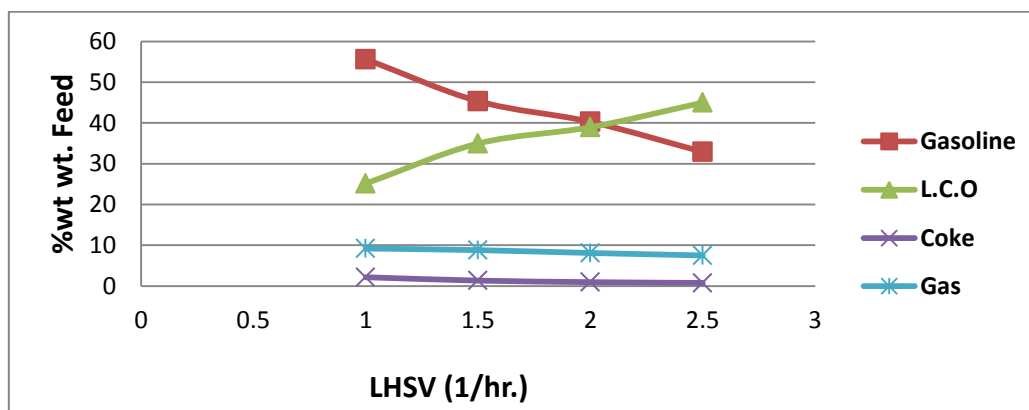Fig. 3: Effect of LHSV on thermal cracking products yield at 480 ℃

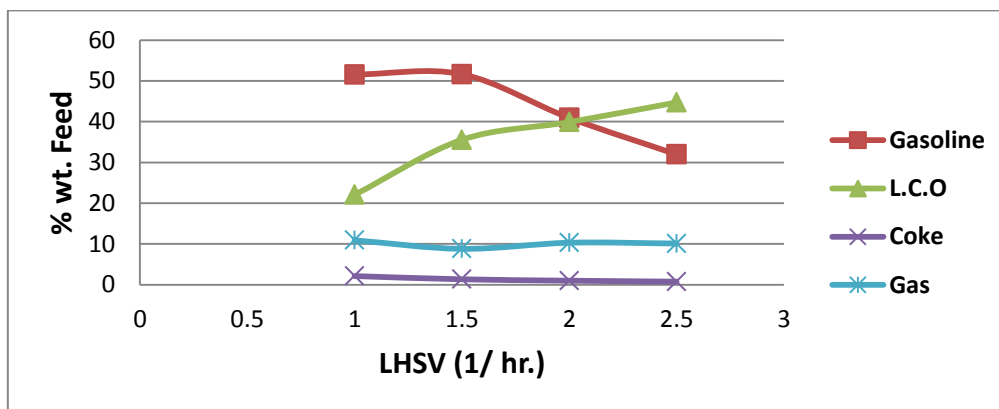Fig. 4: Effect of LHSV on thermal cracking products yield at 500 ℃

Fig. 5: Effect of LHSV on thermal cracking products yield at 520 ℃

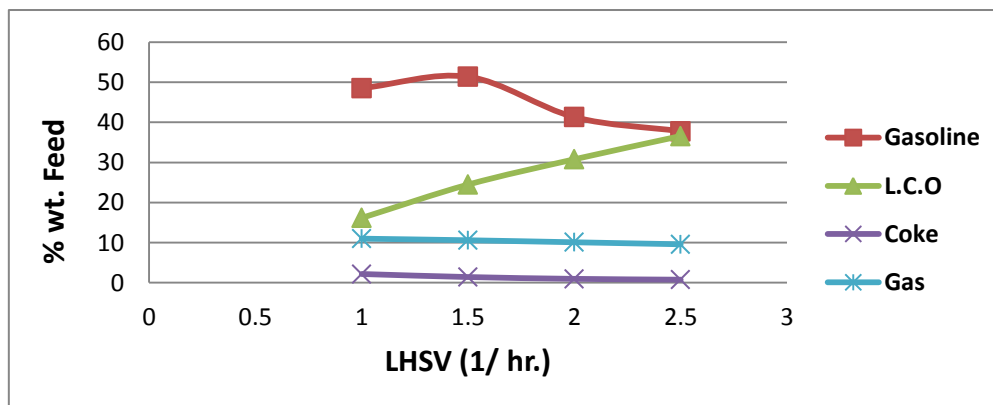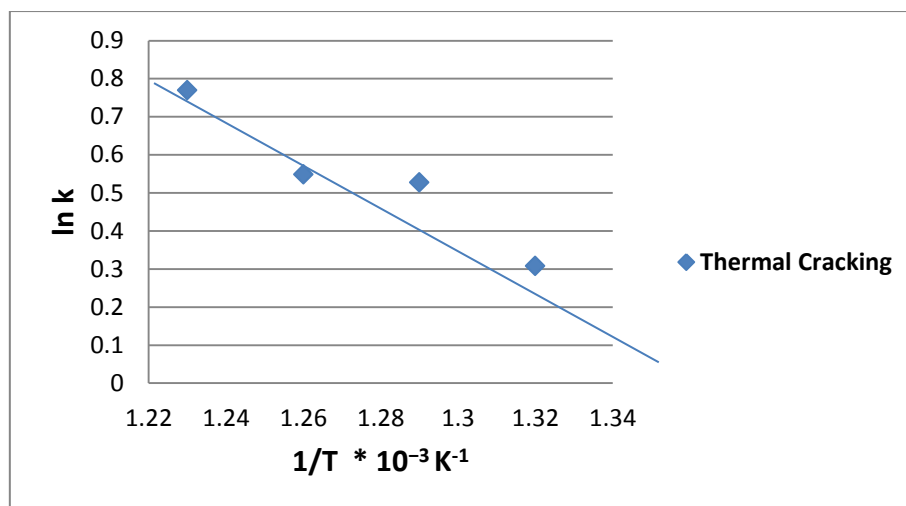
Fig. 6: Effect of LHSV on thermal cracking products yield at 540 ℃

Fig. 7: Plot of lnk vs. $\frac{1}{T}$

The effect of temperature ranges (480-580) on the slack wax conversion and the yield of gases, gasoline, light cycle oil and coke were studied at LHSV range 1.0-2.5hr^{-1}.

The slack wax conversion increases with increasing temperature. This may be due to acceleration inter molecular motions, assisting the transformations of the reactants into new compounds and thus enhancing the rate of chemical reaction, as mentioned also by Decroopcq [9].

Kinetic of Thermal Cracking

The reactions proceeding in thermal cracking obey first order shown in Equation 1 [10].

The integral method of analysis always puts a rate of equation to the test by integrating and comparing the predicted concentration (C) versus time (t) curve with the experimental concentration (C) versus (t) data [11].

$$-r_A = k \, C_{A=} -\frac{dc_A}{dt} \qquad \ldots(1)$$

The fractional conversion X_A is defined as the fraction of reactant converted into product. For constant density, system volume does not change:

$$C_A = \frac{F_A}{V} = \frac{F_{Ao(1-X_A)}}{V} = C_{A_o}(1-X_{A)} \qquad \ldots(2)$$

Differentiation Equation 2 gives:

$$-dC_A = C_{Ao} dx_A \qquad \ldots(3)$$

And hence Equation 1 becomes:

$$\frac{dx_A}{dt} = k \, (1 - x_A) \qquad \ldots(4)$$

Integration gives:

$$k = \frac{1}{t} \ln \frac{1}{1-X_A} = \frac{vo}{V} \ln \frac{1}{1-X_A} = \frac{F_{A_O}}{V C_{Ao}}$$
$$\ln\frac{1}{1-X_A} \qquad \ldots(5)$$

The activation energy of cracking reactions can be estimated by Arrhenius equation $k = k_O e^{\frac{-E}{RT}}$ was 80.18 kJ/ mole. Plotting ln k versus 1/T as shown in Fig.7 gives a straight line with slope equal to (-E/R).

The Possibility of Slack Wax Cracking Uses

Properties of light naphtha, heavy naphtha, kerosene and gas oil produced by thermal cracking at temperature 500 ºC and LHSV=1.0 $hr.^{-1}$ are listed in Table 2.

Table 2: The properties of liquid products

Characteristics	Light naphtha	Heavy naphtha	Kerosene	Gas oil
Specific gravity, 15.6 ℃/15.6 ℃	0.698	0.783	0.80	0.885
API gravity	71.05	49.21	44.45	28.38
Sulphur content, wt.%	0.03	0.07	0.092	0.097
Net heat, cal/gr.	11375	11100	10272	11324
Octane number	87.04	85.35	------	-----
Smoke point, mm	-----	-----	30	----
Aniline point, ℃	---	----	----	83
Diesel index	-----	-----	-----	51.5
PONA analysis, wt.%				
N-paraffin	38.64	20.05	35.43	40.49
Iso-paraffin	36.29	16.65	24.32	24.73
Naphthene	5.10	8.18	6.10	5.29
Olefin	19.17	50.20	21.12	17.50
Aromatic	0.75	4.90	13.027	11.98

The light and heavy naphtha obtained by thermal cracking have high octane number and low sulphur content, so it is possible to use these naphtha as a component for automobile gasoline production. Kerosene obtained by thermal cracking low aromatic and sulphur content and high smoke point compared with Iraqi commercial value, so it is easy to be used as a component for domestic kerosene production. The gas oil has high n-paraffin, iso paraffin and diesel index and low aromatic and sulphur content, so it can be used as a good component for light diesel fuel and fuel oil production. The properties of light, medium and heavy lubricating oils produced from thermal cracking are listed in Table 3.

These oils have high viscosity index and flash point and they have very low of ash and carbon residue and acceptable viscosity compared with commercial, but the pour point is very high. Because of the high value of pour point, these fractions should be blended with respective oil fractions; the dewaxing process for pour point is going to decrease.

Table 3: The properties of light, medium and heavy lubricating oils

Type test	Results of thermal cracking			Iraqi commercial value [12]
	Temp. wide distillation, ℃			
	390-430	430-450	450-520	
Viscosity at 40 ℃, Cst.	8.3074	7.0282	------	-----
Viscosity at 100 ℃, Cst.	2.8895	2.5455	3.175	-------
Specific gravity at 15.6 ℃/15.6 ℃	0.795	0.781	0.782	------
Viscosity Index	200.56	193.248	------	95 min.
Pour point, ℃	------	27.8	------	-6
Ash content, wt. %	Nil	Nil	------	-------
Carbon residue, wt.%	0.2559	0.0295	Nil	-------------
Flash Point, ℃	200	200	202.0	200 min.

Conclusions

1- The slack wax conversion increases with the decreasing of LHSV at constant temperature and increases with increasing the temperature.

2- The decreasing of LHSV at constant temperature for thermal cracking

increases the cracking yields of gases, gasoline, and coke and decreases the light cycle oil.

3- The increasing in the reaction temperature for thermal cracking firstly increases the gasoline yield and then higher temperature, over cracking occurance gives lower gasoline yield, while the yield of gases increases.

4- Based on the maximum of the gasoline yield, it could be said that the best cracking temperature was 500 ℃ for thermal cracking, while the best liquid hour space velocity was 1.0 hr^{-1}.

5- The properties of light and heavy naphtha like octane number and sulphur content which are produced by thermal cracking are acceptable compared with these required by Iraqi standard value, so they could be used as a component for automobile gasoline production.

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