

# Deasphalting of Olefin Pyrolysis Fuel Oil by Combination of Chemical–Physical Methods

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## Abstract

This work investigated the effect of different conditions of Pyrolysis Fuel Oil (PFO) thermal cracking of two PFO samples on liquid, solid and gas product yields and asphaltene removal efficiency in a newly designed experimental setup. There is no need to use a catalyst, simple operating system and experiment conditions. The ability to use water as a cheap carrier gas and high asphaltene extraction efficiency without the use of solvents are outstanding benefits of this method in upgrading PFO. The yields of liquid, solid and gas products were compared in various operating conditions and the optimum experimental conditions were obtained. The results revealed the best thermal cracking condition of PFO in terms of liquid yield and asphaltene removal in this setup for samples. The optimum conditions were 390 and 380°C for the reactor temperature of PFO-1 and PFO-2, respectively; 150°C for the temperature of carrier gas and 100 ml/min for carrier gas flow rate. In these circumstances about 70 and 53 wt% of the liquid product, 25 wt% of the solid products, and 5 wt% of the gas product are generated and the asphaltene separation was reached about 95 and 96.5%.

## Keywords

Asphaltene;  
Naphthalene;  
Product yield;  
Pyrolysis fuel oil (PFO);  
Thermal cracking.

## 1. Introduction

The residues of production lines in petrochemical industry, such as pyrolysis fuel oil in olefin plant, are the least valuable produ-

cts so that their upgrading processes have gained worldwide interest which requires the use of units to prevent high yields of coke and more beneficial yields of distillate products in order to convert oil residue into more desirable products. A mixture of high boiling aromatic hydrocarbons, produced as a by-product during pyrolysis of oil fractions is a dark brown to black colored viscous liquid with pour point approximately 15 °C and a distinctive mothball-like odor classified as a hazardous substance with carcinogenic components

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according to EC directives and used as a raw material for manufacturing carbon black or burned as industrial fuels. The pyrolysis fuel oil (PFO) feedstock contains about 30 to 35 (w/w %) of asphaltenes in matrix solution which consists the highest molecular weight and aromatic hetero compounds with aliphatic substitutions, the majority of impurities and hetero elements, and low hydrogen to carbon ratios. Furthermore, it is the most complicated fraction which contains more than thousands different molecules [1-7].

In the last few years, characterization of asphaltene precipitation has been investigated [8-10]. While asphaltenes act as coke precursors which would lead to catalyst deactivation, the complicated macromolecular structure of asphaltene strongly affects upgrading and refining operations and determines the quality and processing effect of PFO to a certain degree. Problems associated with asphaltene precipitation and deposition have been widely reported in the petroleum production and processing industry [11-14]. Enhanced oil recovery techniques have also led to some asphaltene problems. These these compounds could be prone to condensation and coking during processing and would deactivate catalysts.

In recent years, several technologies have been developed for residual oil upgrading and several researchers have been trying to improve the processing technologies of heavy fuel oils by reducing asphaltene because it has been proved that one of the most important problems related to governing processes of these technologies would be high content of resins and asphaltenes.

Thermal cracking processes which could be used in the refining industry, including delayed coking, fluid coking, flexi-coking, visbreaking, and Eureka process, not only do facilitate the operation to have a condition of low pressure and high to moderate working temperatures with no demand for expensive catalysts, but also provide us with a simple robust control operation [15].

It could be possible to remove the asphaltene fraction, as the precursors of coke formation, from heavy and residual feedstock by Eureka process which is a commercially proven thermal cracking process that produces deasphalted liquid product, as a light feedstock and aromatic petroleum pitch, from vacuum residues in order to

produce deasphalted liquid product, as a light feedstock.

Solvent deasphalting (SDA), as another separation process in which the residue is separated by molecular weight (density) instead of boiling point, would require a high volume of solvent which would allow us to deduce the fact that this process cannot be regarded as a beneficial one, from an economic point of view [16]. Asphaltenes are not crystallized and cannot be divided into individual components or narrow fractions.

Thermal cracking of heavy oils, especially the residual feedstock, and investigation of the yields and properties of the product of this process in different conditions and severities have been the point of focus and interest in most of the previously conducted studies [9, 10, 17-20]. Nevertheless, due to the high content of asphaltenes and aromatic compounds in the range of naphthalene in PFO, it is not possible to upgrade this new material (i.e. PFO) in a single step by the currently available methods (such as Eureka process). Therefore, the primary process should include the elimination of these troublesome compounds. However, the use of a new system is necessary in order to resolve the problem of naphthalenic compounds which could eclipse and stop the operation because of their deposition along the path.

The main concern and focal point of this research would be the study of PFO upgrading, olefin plant by-product, and using a newly designed setup in order to remove asphaltene from two PFO samples and, in the meantime, naphthalenes removal from one of the PFO samples to the next upgrading processes and obtain valuable compounds. The innovative aspect of the newly designed experimental setup is the use of a special condenser for the separation of aromatic compounds such as naphthalene because these materials immediately result in condenser congestion during exiting the reactor. This section has not been predicted in previous studies. Therefore, this setup can also be used to refine the compounds containing naphthalene.

While generating the maximum amount of liquid product containing the minimum amount of asphaltene has been another objective of this study, the yields of liquid, solid and gas products have been compared in various operating conditions and an optimum experimental condition is ob-

tained under different experimental conditions, asphaltenes are precipitated in a rejected fuel oil with light alkane precipitants (i.e., n-pentane, and n-heptane) and characterized using some common analytical techniques.

Due to the variety of feed in petrochemical plants such as naphtha, gaseous feeds: propane, ethane, etc., two olefin plants were selected from each category. Having prepared the two samples of PFOs from different Iranian petrochemical Companies, the produced gas, liquid (deasphalted maltenes) and solid fractions characterized by variety of analytical techniques while the obtained naphthalene from PFO-1 is characterized by Gas Chromatography-Mass Spectrometry (GC-MS) solid product containing asphaltene, gas product, and the organic components are analyzed using X-Ray Fluorescence (XRF), gas chromatography and Detailed Hydrocarbon Analysis (DHA), respectively. Physical properties of the liquid product include n-heptane insoluble fraction, refractive index, density, and viscosity were investigated.

## 2. Experimental Methods

### 2.1. Materials

The proposed PFO samples (sample #1: PFO-1 and sample #2: PFO-2) were waste materials which were obtained from two different Iranian petrochemical olefin plants. PFO-1 and PFO-2 were the by-products of olefin plants with naphtha and gas mixture feedstock, respectively. Given that the feeds of the petrochemicals producing these two PFO samples are different, their characteristics, including the asphaltene content, are also different. All chemical solvents such as pentane, heptane, acetone (with 99% purity), used in the present investigation, were purchased from Merck. Steam was produced from deionized water. The purification of N<sub>2</sub> cylinder was 99.9%.

### 2.2. Experimental setup and procedure

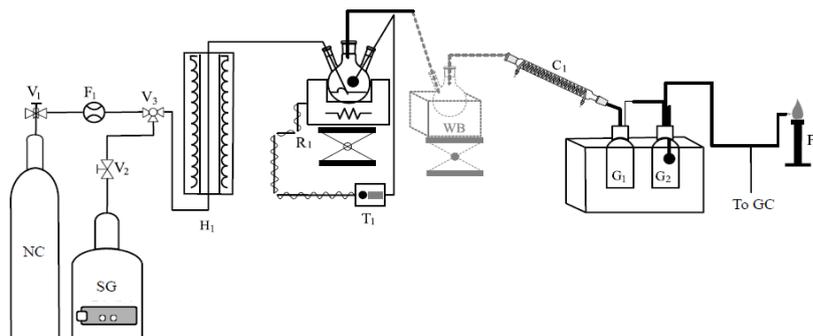
The PFO thermal cracking experiments were performed using a bench scale experimental setup, a detailed schematic diagram of which is shown in Fig. 1. Three-neck Pyrex flask, with an internal capacity of 500 ml, which was subjected to a pre-

specified inside temperature in a heating mantle equipped with a temperature controller and insulated with glass wool jacket, was used as a thermal cracking reactor. In each test, the reactor was loaded with 100 g of PFO. Pre-heated carrier gas (N<sub>2</sub> or Steam) stream was injected at a constant flow rate into the reactor to evacuate the products immediately after formation and to mix the feed. Two design approaches were applied for two different PFO samples upgrading process. In the first setup, three condensing steps were utilized. Because PFO-1 contains compounds, which caused condenser congestion, and for the separation of these compounds it is necessary to use a balloon condenser placed before the tube condenser. In the first condenser (WB), which was immersed in a water bath, a two-neck flask was utilized to remove the high-temperature condensable product portion of PFO-1 to prevent plugging of the coil condenser. The remained non-condensed vapor was passed through the condenser (C<sub>1</sub>) and ice-water bath (G<sub>1</sub>, G<sub>2</sub>) to recover light fractions of the oil product. The non-condensable gas products and inert carrier gas (N<sub>2</sub> gas) were purged to flare. In the second setup, only the first condenser (WB), was eliminated from the upgrading. This setup was utilized for upgrading of PFO-2. Each experimental run produced three products: liquid, gas and solid oil.

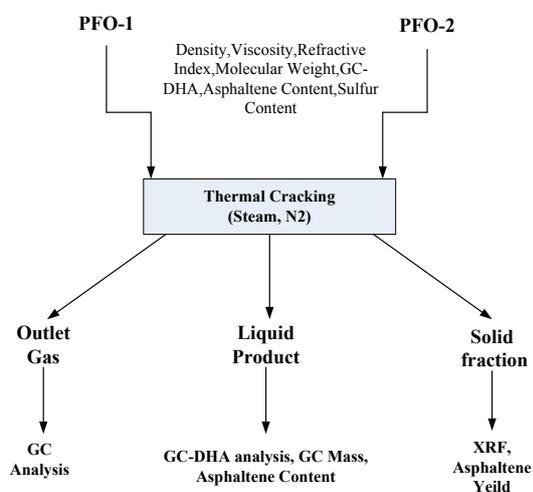
The reactor was purged with N<sub>2</sub>, for leakage testing, and then it was subjected to a pre-specified inside temperature. The effect of four parameters including reactor temperature (350-450 °C), N<sub>2</sub> flow rate (50,100, 150 ml/min), carrier gas nozzle position, and carrier gas type (N<sub>2</sub> or steam) on asphaltene removal rate from PFO, time of thermal cracking, and product yields were studied.

### 2.3. Characterization methods

The n-heptane insoluble fraction of PFO and liquid product, as the asphaltene fraction, density, refractive index (ATAGO NAR-1L LIQUID appending ASTM D1218) and viscosity (Normal ab serial 75 in a bath of wisdom model wvb-30 appending ASTM D 446) of liquid products were determined according to ASTM standards D3279, D1481, D1218 and D445, respectively. The viscosity of liquid products was measured three times and an average value of the measured viscosity data was noted.



**Figure 1.** Schematic diagram of thermal cracking experimental setup: (V-1) N<sub>2</sub> Regulator, (V-2, and V-3) Valve; (SG) Steam Generator; (F-1) Gas Flow meter; (H-1) Carrier gas pre-heater; (R-1) Thermal Cracking Reactor; (T-1) Reactor Temperature Controller; (WB) Water Bath; (C-1) Condenser; (G-1, G-2) collect bottles for liquid product; (F-2) Flare.



**Figure 2.** Schematic diagram of characterization methods

The PFO samples and liquid hydrocarbon products composition were determined by gas chromatography (GC-DHA; Varian CP-3800, capillary column SilPona CB) equipped with flame ionization detector (FID), along with GC-mass spectroscopy (GC-MS; Varian CP-3800, Column CP-Sil 8) for quantitative and qualitative analyses of compounds in the fraction, which was separated as naphthalene at 215-225 °C. In order to prevent GC contamination, a filter was installed before it so as to collect a small amount of unconverted liquid hydrocarbons. The concentrations of gas hydrocarbon products were determined by gas chromatography (GC; Agilent-7890A, column HP-AL/S), equipped with three detectors: FID for detection of CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, etc.; thermal conductivity detector TCD-1 for detection of N<sub>2</sub>, Ar,

CO, and CO<sub>2</sub>; and TCD-2 for detection of H<sub>2</sub> and He. All characterization methods which were used in this study are shown in Fig. 2.

### 3. Results and Discussion

#### 3.1. Reactor tests

Due to the difference in composition of the two PFO samples, different results were observed during their upgrading tests. PFO-2 contained some water which should be removed during the first stage of upgrading. After adjusting the temperature of the mantle at 200 °C, reactor temperature continuously increased to reach 100 °C, which is the temperature of PFO's water separation. At the temperature range of 70-80 °C, a trace of vapor was observed in the condenser. A continuous weak flame which was related to the burned compounds was also detected. Increasing temperature to about 90 °C resulted in observation of a yellow liquid in the condenser, in addition to water vapor which resulted in reduced flame volume. During water separation stage, the temperature remained constant for about 10 min.

After removal of all water, the liquid product was collected at a temperature about 115 °C. A brown liquid has been produced due to upgrading reactions which flows at a temperature range from 120 °C to 200 °C, in the condenser.

A decreasing temperature gradient was observed in the aforementioned reactions which could be proved to be a result of some endothermic reactions in some temperature ranges. At the end of PFO-2 test, the water in the liquid product was

isolated and the rates of dry products were reported. The deasphalting test of PFO-1 was different from PFO-2 test may be because PFO-1 had been dried.

In these experiments, unlike PFO-2 tests, at a temperature of about 220 °C, flames could be seen. Tests duration of the two samples were almost similar.

Generally, increasing the temperature and the carrier gas flow rate led to the reduction of test duration. In carrier gas flow rate of 100 ml/min, after 100 min of the test, flame was observed. The results indicated that, although carrier gas did not have any role in reactions, it acted like a mixer and increased the penetration rate of molecules and test rate.

### 3.1.1. Reactor temperature effect

The liquid, gas and solid yields (wt %), obtained at the different temperatures, are presented in Fig. 3. It can be seen that the liquid yield increased by temperature while the solid yield decreased with an increase in the temperature. With increasing temperature, physically breaking the large molecules bonds into smaller ones would be easier. This factor facilitates the production of light liquid samples.

The gas yield remained partly constant by temperature; however, the minimum portion of products devoted to gas and the lowest gas was obtained at 380 °C and 390 °C. These observations showed that temperature is one of the most important factors affecting thermal cracking efficiency. This also corresponds to Sawarkar et al. results [21]. Based on the obtained results, 390 °C and 380 °C were chosen as operating temperatures for upgrading of PFO-1 and PFO-2, respectively

### 3.1.2. The effect of carrier gas nozzle location

Two different positions are considered for carrier gas nozzle in this study. It is an important process parameter affecting the products' yield.

After fixing the other factors, the nozzle location parameter was placed out of reaction feed for the first experiment series, but it was located into the feed in the other test series. It is observed that

putting down nitrogen in the feed could result in a significant increase in the rate of liquid product, (as shown in Fig. 4). Since PFO samples are highly viscous, putting down carrier gas nozzle in the feed helps uniforming and homogenizing the sample during cracking which has resulted in better cracking operations due to inert gas flow and bubble formation within the sample.

### 3.1.3. Carrier gas flow rate effect

The carrier gas flow rate is one of the effective parameters which influences products yield. Yield of liquid, gas and solid products, as a function of N<sub>2</sub> flow rate, are shown in Table 1. By increasing the N<sub>2</sub> flow rate from 50 to 150 ml/min, the liquid yield increased at first and then it slightly decreased. Solid and gas products yield decreased with increasing N<sub>2</sub> flow rate. The best experimental condition is observed when the liquid yield is at its maximum level and the asphaltene quantity is at the lowest level. In this work, the high quantity and quality of the liquid product were achieved at 390 °C and N<sub>2</sub> flowrate of 100 ml/min.

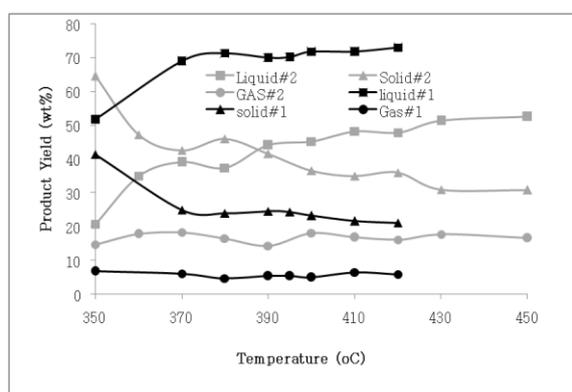
N<sub>2</sub> was replaced by steam in some experiments with optimum condition (390 °C & 100 ml N<sub>2</sub>/min). Given that the inert gas has not taken part in cracking reaction. The results showed that the steam did not highly change the products yields. For example, the asphaltene quantity of the liquid product was higher when steam was used as carrier gas. Since the PFO samples are highly viscous, increasing the carrier gas flow rate helps uniforming and homogenizing the sample during cracking which has resulted in better cracking operations due to inert gas flow and bubble formation within the sample.

## 3.2. Characterization results

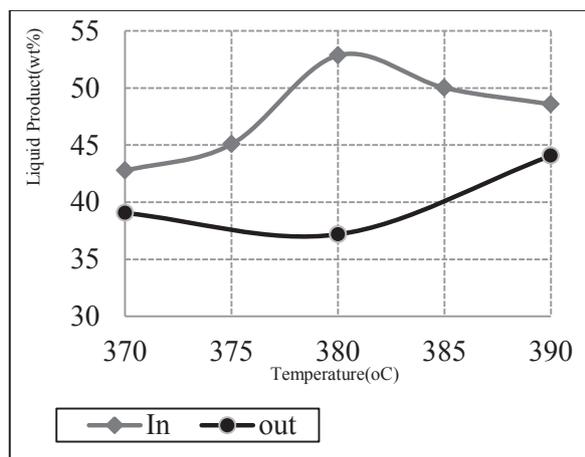
### 3.2.1. Feedstock characterizations

The asphaltene contents of original samples were measured using ASTM standard D 3279-01 and filter papers (Whatman No. 2, England) with a pore size of 2 μm [22]. First, one volume of PFO was mixed with 40 volumes of liquid precipitant (either n-pentane or n-heptane). It is worthwhile to note that different liquid precipitant-to-oil volume ratios were tested to study the volume-ratio effect on the asphaltene yield. The purity of both

n-pentane and n-heptane, used as respective precipitants, were 99.9%. It is found that precipitant has a strong influence on the yield and physico-chemical properties of the precipitated asphaltenes and these new techniques provide us with a promising opportunity in order for the rejected fuel oils to be transformed into the feed of petrochemical plants in a beneficial economic perspective.



**Figure 3.** Dependence of gas, liquid, and solid products yield on reactor temperature.



**Figure 4.** Changes in the liquid product yields of PFO at different temperatures by changing the nozzle position.

The PFO-n-pentane or n-heptane mixture was agitated using a magnetic stirrer (SP46925, Barnstead/Thermolyne Corporation, USA) for 12 h and then filtered with 2  $\mu\text{m}$  pore size filter papers (Whatman, England). The filter cake, mainly composed of precipitated asphaltenes, was rinsed with a liquid precipitant. The rinsing process continued until the precipitant, which comes out of

the filter, lost its color. The precipitated asphaltenes were slowly dried at 100 °C, on the heated magnetic stirrer until their weight stop changing followed by reading of an electric balance (Mettler Toledo, Canada). On the other hand, the filtrate was distilled at the boiling-point temperature of either n-pentane or n-heptane, under the atmospheric pressure for at least 2 h. The remainder was the deasphalted heavy oil (i.e., maltenes).

**Table 1.** Yield of liquid, gas and solid products (wt%) as a function of N<sub>2</sub> flow rate (ml/min).

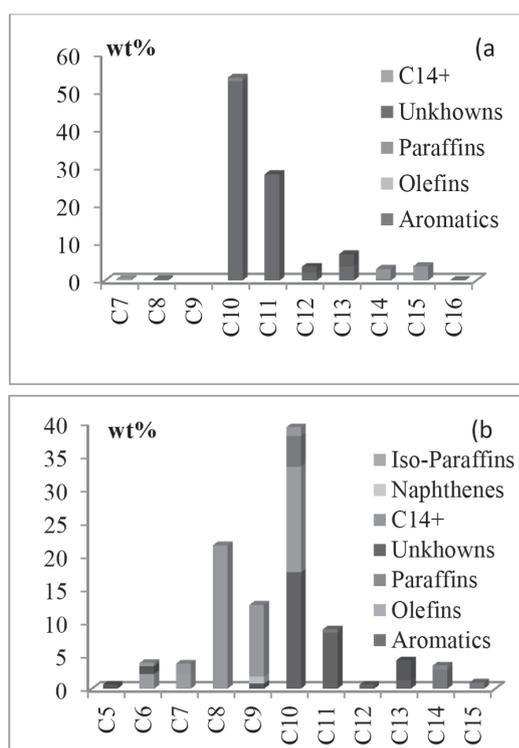
	N <sub>2</sub> Flow	50	100	150
Liquid Yield	PFO-1	70	73	72
	PFO-2	41	53	51
Solid Yield	PFO-1	24	22	22
	PFO-2	45	35	35
Gas Yield	PFO-1	6	5	5
	PFO-2	14	12	15

For GC-DHA analysis of the feedstock, each sample was mixed with acetone for 24 h. After filtration, dissolved portions of all samples were used for analysis. The composition of PFO fraction was very complex and it was a mixture of paraffins, naphthenes, aromatics, and olefins. Table 2 shows the most common components along with the physicochemical properties in the two proposed feedstocks. According to Table 2, sulfur content of PFO-1 was more than PFO-2 and aromatics content of PFO-1 was much more than PFO-2. However, PFO-2 had significant water content whereas the other feedstock did not have any water content. Due to this reason, for n-heptane insoluble fraction content of PFO-2 two values, wet and dry, were reported. The n-heptane insoluble fraction can be considered the same as the asphaltene content. Hence, it is possible to use asphaltene content as a comparison index of the two feedstocks. This fraction contains asphaltene and compounds that would be capable of being converted to asphaltene in the future. It was observed that PFO-2 had a high volume of olefin and iso-paraffin compounds. It should be noted that, in case of PFO-1, the quantity of olefines was negligible and there was no iso-paraffins. Although the compositions of these feedstocks are so different, their dry asphaltene contents are almost the same.

**Table 2.** PFO samples properties.

Properties	PFO-1	PFO-2
S(ppm)	1470	1038
Aromatics (%wt)	86.492	27.841
Olefines (%wt)	0.344	20.371
Paraffins (%wt)	1.77	8.873
Naphthenes	-	1.038
Iso-paraffins	-	35.766
Asphaltene (%wt, in C <sub>7</sub> )	31.56	19 <sup>a</sup>
		31.7 <sup>b</sup>

<sup>a</sup> in wet PFO, <sup>b</sup> in dry PFO



**Figure 5.** Distribution of hydrocarbon compositions of feedstock obtained from DHA analysis: (a) PFO-1 and (b) PFO-2.

Detailed hydrocarbons information of the two feedstocks, obtained from GC-DHA analysis, are illustrated in Fig. 5. As it is shown in Fig. 5(a) most of the organic compounds in PFO-1 are C<sub>10</sub> and C<sub>11</sub> aromatics with high content of naphthalene and methylnaphthalene, whereas Fig. 5(b) indicates that most hydrocarbons in PFO-2 are C<sub>10</sub> hydrocarbons composed of aromatics, olefins, paraffins and iso-paraffins and larger amounts of iso-paraffins are available in C<sub>8</sub> and C<sub>9</sub> groups.

### 3.2.2. Liquid product characterization

#### Property analysis

The results of bulk analyses performed on the liquid product, obtained from the thermal cracking in different conditions, can be found in Table 3. As it can be seen, by increasing the temperature, in various N<sub>2</sub> flow rates, density, viscosity, refractive index and molecular weight of liquid product did not changed significantly while the optimum asphaltene removal rates from PFO-1 and PFO-2 (i.e. 98% and 96%) were obtained at 390 °C and 380 °C and 100 ml/min of N<sub>2</sub> flow rate.

In addition, viscosity range of a typical diesel fuel is approximately between 1-3.8 mPa.s, which is similar to the liquid product of this study. Sulfur content of liquid products of PFO-1 and PFO-2 are about 1170 and 606 ppm, respectively. The viscosity, density, average molecular weight and refracting index of liquid product in the best cracking conditions, are 1.79-2.82 cSt, 1 g/cm<sup>3</sup>, 201-205, and 1.6, respectively.

#### DHA analysis

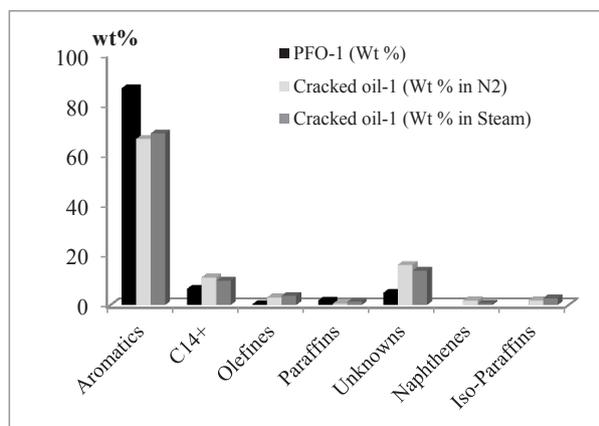
Figs. 6 and 7 illustrate the results of GC-DHA analysis for the liquid products obtained from thermal cracking in the presence of N<sub>2</sub> and steam, as two types of carrier gases. Figs. 6 and 7 are related to PFO-1 and PFO-2, respectively. After cracking, aromatic amounts of liquid products, obtained from PFO-1, decreased to about 67% wt. In the presence of steam, the production of aromatic, olefin, paraffin and iso-paraffin increased while the amount of unknown hydrocarbons decreased, as shown in Fig. 6. According to Fig. 7, after thermal cracking of PFO-2 in both states, aromatics content increased and, at the same time, the rate of iso-paraffins decreased significantly. Also, in the presence of steam, the production of aromatic and unknown hydrocarbons increased while the amount of olefin, paraffin and, iso-paraffin decreased.

An important point to keep in mind is that the represented GC-DHA data for the feedstocks were related to their portion which dissolved in acetone and injected to the GC analyzer. On the other hand, the obtained liquid products were injected directly to the instrument and their results about

total compounds which were produced after cracking. Thus, the proposed heavy residues were thermally cracked successfully. DHA analysis data of proposed feedstocks and their liquid products, which obtained in both states, are listed in Table 4.

### 3.2.3. GC-Mass analysis of Naphthalene

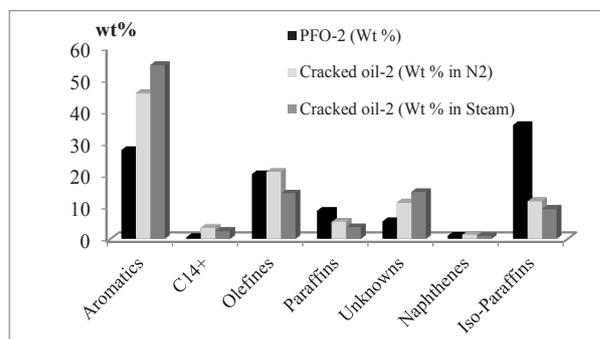
Naphthalene is the most abundant single constituent of coal tar, a volatile product from destructive distillation of coal, and it is also formed by modern processes for the high-temperature cracking (breaking up of large molecules) of petroleum. It is commercially produced by crystallization from the intermediate fraction of condensed coal tar and the heavier fraction of cracked petroleum. It was found out that the high-boiling residue of oil contains naphthalene in admixture with small quantities of  $\alpha$ -methyl naphthalene,  $\beta$ -methyl naphthalene and 1,6-dimethyl naphthalene [23].



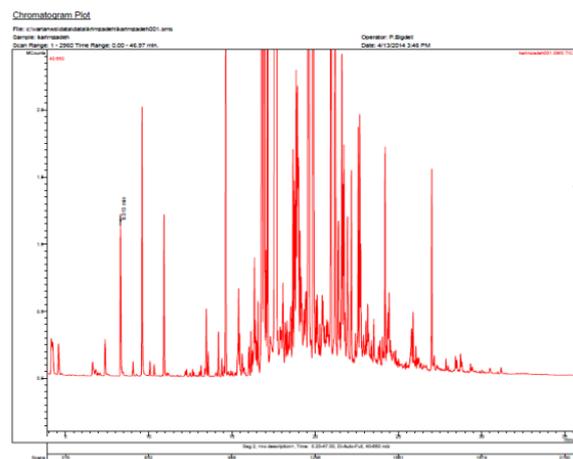
**Figure 6.** Distribution of hydrocarbons by Group Type (DHA analysis) in PFO-1 and the liquid products obtained from thermal cracking in the presence of N<sub>2</sub> and steam.

In order to evaluate compounds in the fraction, which was separated as naphthalene during thermal cracking of PFO-1 at 215-225 °C, GC-Mass analysis was used. Fig. 8 illustrates the results of GC-Mass. According to the results of GC-

Mass (Fig. 8) these compounds can be naphthalene, methyl naphthalene, ethyl naphthalene, and azulene. The amount of Naphthalene is 31.33 wt% and 29.93 wt% of total aromatic with N<sub>2</sub> and steam as carrier gas, respectively. Given that naphthalene is colorless, azulene is a dark blue isomer of naphthalene and ethyl naphthalene has light brown color; thus, the separated naphthalene fraction was light green.



**Figure 7.** Distribution of hydrocarbons by Group Type (DHA analysis) in PFO-2 and the liquid products obtained from thermal cracking in the presence of N<sub>2</sub> and steam.



**Figure 8.** GC-Mass analysis results of naphthalene

**Table 3.** Cracked oil products characterization results

<b>Experiment condition</b>						
T °C	Gas flow (ml/min)	Gas	$\mu$ @167°F (cSt)	RI @100°F (nd)	$\rho$ g/cm <sup>3</sup>	AR%
<b>PFO-1 results</b>						
370	100	N <sub>2</sub>	1.01	1.59	1	92
380	100	N <sub>2</sub>	1.05	1.59	1	92
390	100	N <sub>2</sub>	1.03	1.59	1	98
395	100	N <sub>2</sub>	1.05	1.59	1	95
400	100	N <sub>2</sub>	1.07	1.59	1	94
410	100	N <sub>2</sub>	1.07	1.59	1	88
390	150	N <sub>2</sub>	1.09	1.59	1	95
390	50	N <sub>2</sub>	1.02	1.58	1	93
390	100	Steam	1.04	1.59	1	90
<b>PFO-2 results</b>						
380	100	N <sub>2</sub>	1.13	1.60	1	91
380	100	N <sub>2</sub>	1.19	1.60	1	95
380	100	N <sub>2</sub>	1.26	1.60	1	93
380	100	N <sub>2</sub>	1.22	1.60	1	92

T=Temperature,  $\mu$ =Viscosity, RI= Refractive Index,  $\rho$  =Density, AR=Asphaltene Removal

**Table 4.** DHA analysis of the cracked oils (wt %).

Type	PFO-1	PFO-2	1	2	3	4
Aromatics	86.5	27.9	66	68.4	45.6	54.5
C <sub>14+</sub>	6.5	0.59	11	9.6	3.5	2.5
Olefines	0.34	20.4	3	3.6	21	14.2
Paraffins	1.8	8.9	0.5	1.3	5.4	3.7
Unknowns	4.9	5.5	16	13.7	11.4	14.7
Naphthenes	-	1	2	0.6	1.3	0.9
Iso-Paraffins	-	35.8	2	2.7	11.8	9.4

1: oil-1in N<sub>2</sub>, 2: oil-1in Steam, 3: oil -2 in N<sub>2</sub>,  
4: oil -2 in Steam

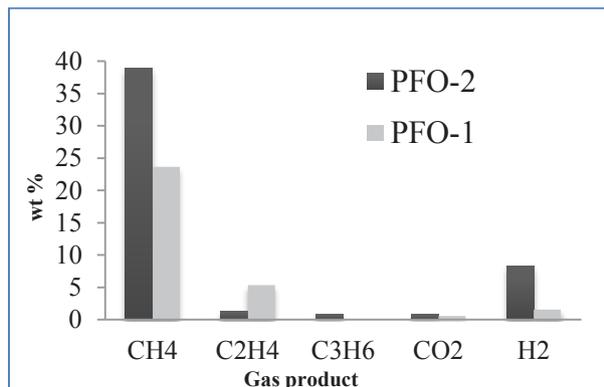
### 3.2.4. Outlet gases characterization

Drawing a comparison between the outlet gases, obtained from thermal cracking in the presence of N<sub>2</sub> and steam, as two different carrier gases, a small amount of CO<sub>2</sub> was observed. It is also observed that, when steam was being used, methane, ethylene and hydrogen production showed an increasing trend (Fig. 9). As a result, it can be concluded that thermal cracking with steam is an efficient upgrading technique.

### 3.2.5. Precipitation yield measurements for water-free liquid product

It is found that the yields and properties of the precipitated asphaltenes and the remaining mal-

tenes strongly depend on the specific precipitant process as well as the employed asphaltene separation conditions. As mentioned above, the n-heptane insoluble fraction content of PFO-1 and PFO-2 were 31.56 % and 31.7%, respectively. After cracking process, the measured asphaltene content of the water-free liquid product, obtained using thermal cracking under optimum conditions, was 0.68 up to 2 wt%. For each sample, the repeatability of the measured asphaltene content was within  $\pm 0.5\%$  of the reported yield data. The optimum asphaltene removal rates of PFO-1 and PFO-2 were 98% and 96%, at 390 °C and 380 °C, respectively.



**Figure 9.** Comparison of weight rates of outlet gases (H<sub>2</sub>, CO<sub>2</sub>, and C<sub>1</sub>-C<sub>3</sub>) for different samples in the presence of steam

#### 4. Conclusion

This work investigated the effect of different conditions of PFO thermal cracking of two PFO samples on liquid, solid and gas product yields and asphaltene removal efficiency in a newly designed experimental setup and, at the same time, produced naphthalenes as valuable compounds from one of the PFO samples.

The ability to use water as a cheap carrier gas and high asphaltene extraction efficiency without the use of solvents, no need for catalyst, and simple operating system and experimental conditions are outstanding benefits of this method for upgrading PFO.

The results showed that liquid yield increases with increasing temperature while the solid product decreased

The obtained results showed That the best thermal cracking condition of PFOs were 390 °C and 380 °C for the reactor temperature of PFO-1 and PFO-2, respectively; 150 °C for the carrier gas temperature and 100 ml/min for the carrier gas flow rate. In these circumstances, about 70 and 53 wt% of the liquid product, 25 wt% of the solid products, and 5 wt% of the gas product are generated while the asphaltene separation reached about 95 and 96.5%. In addition, viscosity and molecular weight of the liquid product vary between 1.79 to 2.82 cSt and 201 to 205 g/mol, respectively. Density and refractive index of liquid product were 1 and 1.6, respectively.

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