

Upgrading options heavy grades of oil from the Algerian oil ^{final}

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Abstract

The global demand for petroleum products is increasing year by year quantitatively and qualitatively, due to population growth and the desire to speed up economic growth of all countries especially in developing; which Algeria belongs to.

Besides the clear products supplied by the fractionation of crude oil, there are a number of heavy petroleum products obtained from the secondary treatment, especially in the context of the protection of the environment and which are not the proper use; they are often used as components of fuel oil. These products are among other atmospheric and vacuum residues, heavy distillates from catalytic cracking, aromatic extracts or else the deasphalted vacuum residue, more known as the deasphalted Oil (DAO).

Now all the refineries are equipped hydrotreating facility to reduce the content of various pollutants in these products on one hand, and methods thermo catalytic molecular rearrangements aimed transform these residues wholes and fractions heavy in market value of products most important on the other hand. Consequently, the choice of adequate processes is a major challenge for oil refineries.

The objective of this work is to value these heavy cuts available in abundant quantities in Algerian refineries by their different compounding proportionalities between aromatic extracts oils manufacturing facilities of Arzew refinery and the vacuum residue obtained from the latter, as well as the residue of the catalytic cracking refinery Adrar for their efficient use as components suitable fillers for thermal or catalytic processes. Our work is limited to the valuation of these products by studying the implementation of the catalytic cracking process which is the most suitable method and is the only one that exists in Algeria.

Keywords: aromatic extracts; vacuum residue; catalytic cracking

1. Introduction

In recent decades and following the requirements of more and more severe, particularly in terms of environmental protection the and after the passage strongly to nuclear, natural gas and renewable sources that are in rapid development without forgetting coal, there has been a sharp decline in heavy fuel oils consumption in the world, which should go on down a few years. Whereas according to the International Energy Agency (IEA) the demand for petroleum products of high value such as fuels and lubricating oils will increase by 88% by 2030 [1] Therefore the oil compared to other the existing energy currently still will long remain competitive energy source used by man.

Face of this urging in these products mentioned should be associated the production to consumption. Thus it is necessary to modify the composition of produce are not valid obtained by simple distillation or other process and to do this additional operations

Therefore, atmospheric distillation or vacuum residues, which were part in the formulation of heavy fuel oils are used in heavy industry such as fuel for the production of electrical energy. They are generally highly viscous mixed with lighter gas oil before being sold.

In order to upgrade the heavy fuel oils and other residues, and get to satisfy the increasing demand for high-value oil products such as fuels, distillates, and lubricating oils[2]

The refining industry has been profoundly restructured. With this the end in view many refineries are closed or upgraded to new conversion units which indeed have greatly reduced or even eliminate the production of heavy fuel. Indeed maximize the yield of clear liquids produced from the various processes has become a major priority for refiners.

On the other hand, environmental specifications have increased and have become increasingly stringent to all petroleum products including heavy products and residues. [3]

To meet these requirements and these radical changes, and also convert these heavy products to light products such as fuels, advanced technology in conversion processes have been developed and expanded rapidly in refining.

This had involved considerable scientific research for laboratories as well as heavy investment. Consequently, the choice of suitable process has become an important challenge for oil refineries.

Several conversion processes were developed either thermally or catalytically, using different heavy loads, with low sulfur content or previously hydro treated to obtain valuable products quantitatively and qualitatively and at different degrees. [4]

Whether thermal or catalytic processes, their role is to break the heavy molecules into lighter molecules. Loads for thermal processes [5-6] are generally atmospheric residue to yield clear fuel, as for vacuum residue whose aim is to reduce the viscosity to produce a fuel for industrial use hence the name visbreaking. In addition, two technologies have been developed to value of heavy and extra-heavy products of high value light products. It is the technology of carbon rejection and hydrogen addition technology. [3,7-8]

The approach of carbon rejection of technology consists of improving the residue rejection of carbon in the load, thereby reducing the overall carbon of the product compared with hydrogen addition technology. In this context it is to break down the heavy molecules which are generally-Nuclear Poly Aromatics (PNA) into lighter molecules by non-catalytic thermal methods generally using low pressures. These residues are generally heavy distillates from coking, residue fluid catalytic cracking of products or advanced visbreaking (visbreaking Advanced) [9]

Thermal cracking, coking and visbreaking which are part of this channel may receive loads which Conradson carbon content up to 20% and a metal content of up to 10 000 ppm (Ni + V). Note that the operating costs of these processes are relatively cheap, but the yields are low light products.[1]

Thermal cracking is one of the first conversion processes used in the oil industry, and has been used since 1913. It was originally intended for fuel production, but after the discovery of the CC, thermal cracking has oriented to other applications such as coking, visbreaking.

Also in this context a technology called Aqua-conversion was developed in Venezuela PDVSA-Intevep with FW and UOP. [10]. It consists of an improved version of Visco-reduction process to reduce both viscosity and density of heavy crude fractions, making a much larger conversion than that used conventional Visco-reduction visbreaking.. However, so far this technology has not been proven in commercial installations.

The second method under the carbon release technology is the solvent deasphalting. This is the only physical separation method where the carbon is rejected from the heavy petroleum fraction such as vacuum residue. In this process, the solvents used, either individually or in mixtures, are generally the light paraffinic hydrocarbons (C3, C4, C5). But now the propane in liquid form (moderate pressure) is widely used to dissolve all the oil, leaving asphaltenes rushing physically separating the vacuum residue into two products, De-Asphalted Oil (DAO) (usually 35 to 75 vol.%) and the De-Oiled Asphalt (DOA) [11-12]. The first effluent is a product of greater value called bright stock and is normally used as the feed of the hydrocracking process and the FCCU process or as a component of a lubricating oil mixture. The De-Oiled Asphalt (DOA) is a rich asphalt aromatic hydrocarbons containing most of the contaminants with high concentrations such as metals, asphaltenes and Conradson carbon [10] can be used as a component, in a delayed coking load or a gasification power [11-12]. It is also a raw material of choice for the production of bitumen for different uses.

The second way of the technologies developed is the technology of the addition of hydrogen. as represented by the following catalytic processes: Catalytic cracking, hydrocracking and hydro-visbreaking. According to the theory of carbonium, this type of breakdown requires considerable energy and can occur in the presence of H + proton donors which are actually the catalyst active centers. Their main characteristic is "quality of products. "

The addition of hydrogen technology gives distillates improved with high efficiency and superior business value than the carbon rejection technology, but requires more investment and the availability of more natural gas to produce the quantities of hydrogen and steam for the process [10].

Regarding the technology of hydrogen addition, there are several commercial technologies worldwide, which are in competition with thermal cracking conversion in the bottom barrel of heavy and extra heavy crude. We can cite [LC Fining](#), [HDH Plus](#), [H-Oil](#), [CanMet](#), and [Shell HyCon](#) among others [10]. All are based on the addition of hydrogen in order to increase the production and the quality of liquid products and the reduction of coke deposition in the process.

Some models can accept feedstock's (atmospheric residue) with a Conradson carbon content up to 38% and about a metal content of 4000 ppm (Ni + V). However the costs of their operations are significantly high and the prices of their finished light products are excessive too. [13-14]

Among these catalytic processes, there are catalytic cracking which is considered as a key element of refining processes, hydro cracking, and hydro-visbreaking processes that are part of this technology. It should be noted that the catalytic cracking is most often used to convert heavy fractions into high value products [15-16].

It is a conversion process that can be applied to a very wide variety of feedstock's, usually vacuum distillate, de-asphalted atmospheric residue known as DAO, vis-breaking distillate, hydro cracking residue and their mixture as well as the by-products of other processes such as lubricating oil extracts and bitumen [17-18]

The Fluidized Catalytic Cracking (RFCC) Residue [1, 19], belongs to the category (hydrogen addition technology), is a similar version to the FCC whose feedstock is a heavy residue. Besides of obtaining high octane gasoline diesel fuel, the method consists of producing a light fraction rich in olefins which are raw materials for the petrochemical industry. This process may take an atmospheric residue with a maximum of 7% Conradson carbon and about 12 ppm of metals (Ni + V) [20-21].

Approximately 24% of the world capacity of residue upgrading belongs to this process. Recently, some manufacturers of catalysts are able to produce catalysts that can tolerate up to about 8500 PPM content of metals (Ni + V) [11,13, 20].

Recently, some have argued catalyst manufacturers produce catalysts that can tolerate up to about 8500 ppm metal contents (Ni + V) and have better slates products [21]

(Yuandong Liu et al. [22] have proposed a hydro treating process for residue upgrading. This process is carried out with a series of reactors. Each reactor has its specific catalyst. It is the same for the function.

Another technology is currently widely studied but still at the laboratory level, it is up in a biological level, using fungi and bacteria selected and assembled in field operations and reproduced in the laboratory. Several institutions have identified microorganisms working between 50 and 65 °C to value the crude at atmospheric pressure, whereas conventional methods require high temperatures and pressures.

There have been studies to characterize the metabolic pathways associated with the desulfurization and the removal of other contaminants. It is expected that the use of bio-technological methods will bring a great impact in the development of crude modernization.

2. Origin of loads of heavy products and composition

A good knowledge of the chemical composition of heavy oil products is required to fully assess their subsequent treatment, given their scientific and industrial impact in the medium and long term, remain unknown. However, the analysis of the chemical composition of these heavy petroleum fractions is the complexity of the original raw material namely heavy crude oil and its components.

According to the SARA method [fig 1](#) by fractionation, crude oils and heavy products such as atmospheric residue vacuum residue, are grouped into four major chemical classes: saturates, aromatics, resins and asphaltenes (SARA). They are based mainly on the difference of solubility and polarity according on their affinity to various organic solvents. [23-24]

The techniques used are generally liquid chromatography (flash chromatography), analytical chromatography (HPLC) or one has lately emerged technology is known as the Iatroscan TLC-FID - Thin Layer Chromatography with Flame Ionization Detection [25]

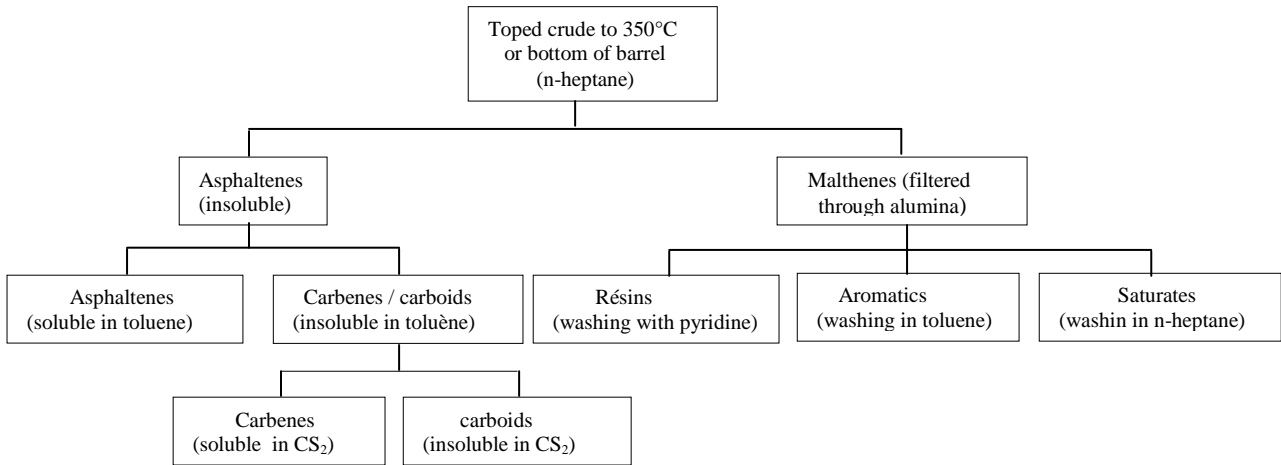


Fig.1 Separation method SARA groups of the bottom of the barrel

The percentages of these various families are highly dependent on the method of separation used, the choice of solvent and the chemical nature of the product to be separated. It is important to note that the analytical results obtained by different methods cannot be compared among them.

It should be noted that despite efforts to analyze these heavy products using different methods, asphaltenes and resins remain as indefinite complex structures in these heavy oil fractions [26].

The vacuum residue obtained from the atmospheric residue is a mixture of such oils, resins and asphaltenes and may contain other heterocyclic compounds. This residue is a raw material of choice for the production of bitumens for many uses. It can also be used as feedstocks to all thermal processes for unsaturated hydrocarbon production needed in petrochemical industry fig2

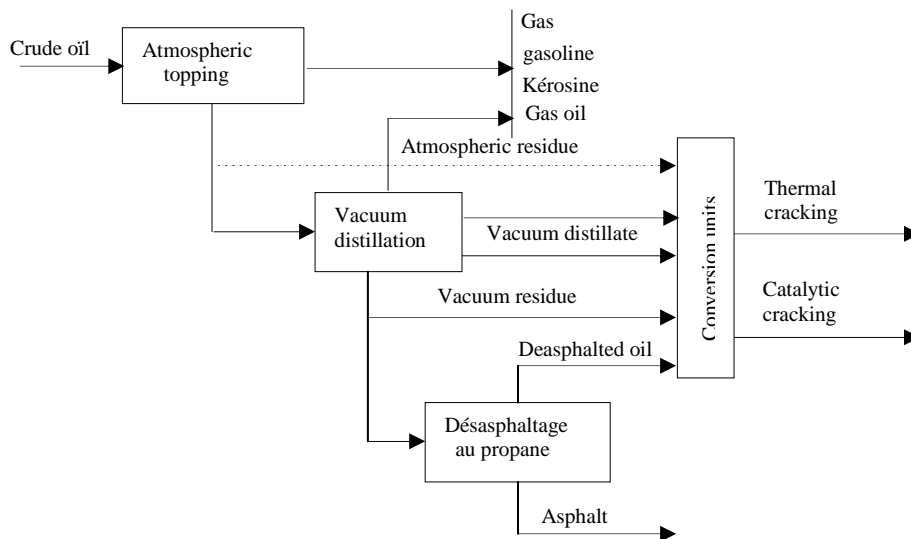


Fig 2. Different loads for conversion units

One of the main characteristics of the typical feedstock for the catalytic process, which directly affects the performance, is the density. It shows to some extent the chemical composition of the feedstock.

Thus, low density characterizes a high hydrogen content, which allows to the load to be easily converted into nobles products such as gasoline and gas. Conversely, a high density indicates a strong presence of aromatics, reflecting a feedstock resistance to crack and an ability to yield heavy aromatic products such as LCO, HCO and slurry [27]

On the other hand, since these oil products essentially consist of hydrocarbon molecules, the density is directly related to H/C ratio. Thus the lower the density of a fraction is much lower than its atomic ratio H/C is large [27]. It should be noted that the residue have low H/C ratio (1.2-1.4), as well as high metal and sulfur contents, as shown in Table 1. Therefore, in order to convert residue into lighter

products one of the most important parameters is to increase the ratio H/C. However, the composition of these residua depends on the origin of heavy crude.

Other characteristics of the feedstock, more or less important, can affect the heat balance of the process and the stability of the catalyst; this is the Conradson carbon that indicates asphaltene content as well as metal content such as nickel and vanadium. Finally, other properties affect directly and indirectly on the heat balance and the efficiency respectively. These are distillation interval and viscosity. A high viscosity and a high endpoint may cause the formation of coke and thereby increasing the temperature of the regeneration and the reduction of conversion [27].

Typically feedstocks are found in the literature characterized by a number of properties conditioning efficiencies and qualities of products. Table 1 gives [27] for example four types of load

Loads examples FCC

Table 1

Charge	A	B	C	D
Type	Distillate	Distillate	Résidue	Hydrotreated residue
Density d_4^{15}	0.937	0.912	0.939	0.926
K_{uop}	11.67	11.91	11.86	12.00
Aniline point (°C)	79	87.4	90.8	97.8
Molecular weight (g/mol)	458	460	612	510
Conradson carbone (% mass)	0.76	0.67	5.6	4.2
Sulphur (% mass)	2.20	0.90	0.90	0.35
Nitrogen (ppm)	1500	1400	2400	1000
Basic nitrogen (ppm)	425	455	688	335
Nickel (ppm)	1.1	0.1	4.0	4.0
Vanadium (ppm)	1.5	0.4	11.0	5.0
Hydrogen (% Wt)	11.56	12.42	12.11	12.43
Distillation TBP (°C)				
5 % mass	358	340	370	347
10 % mass	384	363	396	378
30 % mass	439	403	455	448
50 % mass	476	443	508	506
70 % mass	509	496	577	576
90 % mass	549	571	695	692
95 % mass	566	615	719	733
Viscosity 100°C (mm ² s ⁻¹)	10.3	8.3	25.5	24.8

3. Experimental part

3.1. Formulation of feedstocks for catalytic processes from extracts and vacuum residue from Arzew refinery and the residue of catalytic cracking from Adrar refinery

The objective of this work is to develop these heavy cuts available in abundant quantities produced by compounding different proportionalities between aromatic extracts manufacturing facilities oils Arzew refinery and the vacuum residue obtained from the latter, and the residue catalytic cracking of the Adrar refinery, to their rational use as components suitable fillers for thermal or catalytic processes.

Extracts derived from aromatic extraction from lubricating oil plants are rich in s mainly poly-aromatics compound, and may be adequate sources of feedstocks for the production of carbon black [28]. The latter is an important raw material for various industries: tires production, painting production, ink production and others. Furthermore, their treatment in catalytic cracking may be interesting since they may give birth to gasoline bases that are sought for their high octane number given by their aromatic chemical compositions. For this reason, a detailed study of extracts from selective treatment of oil resulting from local petroleum refineries as a source of aromatic compounds is necessary [28].

In order to follow up on the appraisal of catalytic cracking processes and better understand the behavior of different feedstock, it is necessary to characterize the aromatic extracts obtained from oil production facilities in Arzew refinery and vacuum residua from the same refinery, and heavy

distillate or residua catalytic cracking from Adrar refinery. However, their analysis is difficult because of their nature (opaque and viscous) and complexity.

To track the upgrading processes in catalytic cracking and better understand the behavior of different loads, it is necessary to characterize the aromatic extracts manufacturing facilities oils Arzew refinery and vacuum residue from the same refinery and heavy distillate and residue catalytic cracking resulting from the Adrar refinery. However, their analysis is difficult due to their nature (opaque and viscous) and complexity. The quality of the raw material is assessed by standard methods and empirical relationships characterizing the degree of the load aromatization [29] [30]. This is the characterization factor of K_{UOP} (Watson-Nelson and Smith) [31], the index of correlation of Smith [32], the H/C and the coefficient of aromaticity [33].

It is known that the aromatic content in the extracts and their composition depend on the chemical composition of raw materials, and methods of preparation.

Previous studies have shown that in distillates and extracts obtained by selective purification contain an appreciable amount of oil mixed with aromatic structures paraffino-naphtheno-aromatic. Although the aromatic content in the extracts can reach 60-70% and sometimes up to 85% [34], but the majority of carbon in these compounds are on paraffinic side chains

3.2. Study of extracts from selective treatment of oil fractions

Based on the foregoing, it becomes apparent that the detailed study of extracts of selective treatment of oil fractions as raw materials to feed the catalytic cracking is appropriate.

Fig 3 shows the pattern of products obtained from the processing unit of the oils in the Arzew refinery. For this purpose, a series of products (Table 2) has been selected showing that medium and heavy oil extracts from selective purifying by the furfural may have particular interest, since they possess a relatively high correlation index 75 and 83, respectively. These extracts are also characterized by low sulfur content (0.56 and 0.67 % wt) and coke (1.04 and 1.43% Wt.)

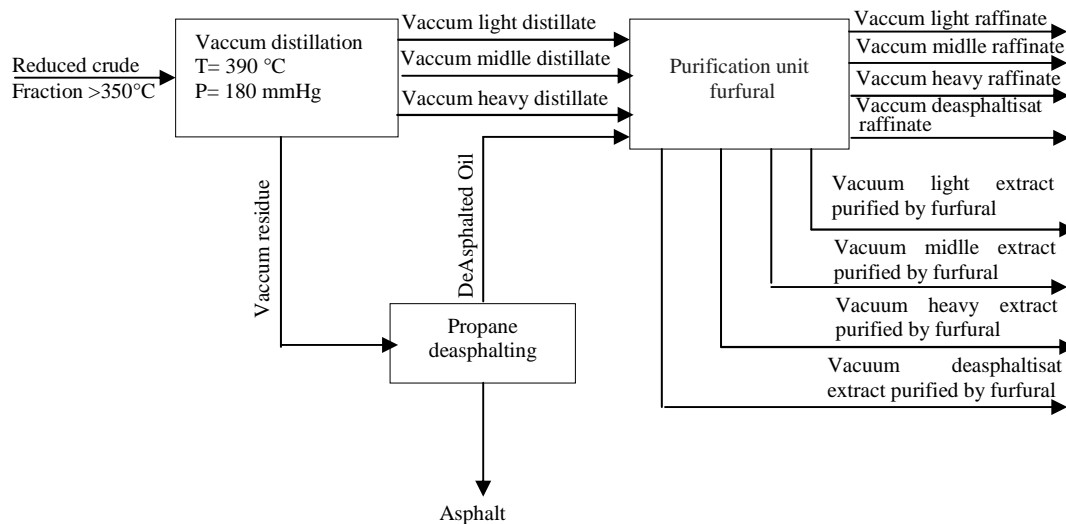


Fig. 3 Schema of the products obtained from the oil treatment unit in Algeria

It should be noted that the extracts from selective treatment of vacuum distillates by furfural have a much higher degree of aromaticity than those similar extracts from the treatment by the phenol and approach in terms of aromaticity to the coker gas-oil and thermal cracking [31].

Deasphalted oil extracts DAO from selective treatment by furfural have qualities much lower. Despite the relatively high content of aromatic hydrocarbons and the high-cycle of average molecules, deasphalted oil extracts have a low correlation index and a very high viscosity (Table 2). Consequently, the chance to use them as raw materials feeding the FCC) is questionable.

However, for their valuation, they can undergo operations of a shallow lightweight thermal cracking for decreasing the viscosity of these products to make them usable as industrial heavy fuel after possible addition of a light diluent (diesel) As regards the other base oil products, none of them, the

degree of aromaticity, meets the standards for catalytic cracking feedstocks. Therefore they cannot be used.

Base oils fractions	Product Characteristics										
	Distillation Range °C	Density d_4^{20}	Sulphur Content % Wt	Carbon Conradson % Wt	Kinematic Viscosity V_{100} mm ² /s	Corrélation Index CI	Structural composition				
							Cycle number		Carbon content % poids		
K _o	K _a	C _o	C _a	C _n							
Vacuum middle extract purified by furfural	310 - 420	0.9656	0.56	0.14	12.0	75	2.85	1.95	67.6	46.2	32.4
Vacuum heavy extract purified by furfural	350 - 510	0.9973	0.67	1.43	33.7	83	3.85	2.45	70.7	44.8	29.6
Vacuum deasphaltisat extract purified by furfural	480 - 520	0.9525	0.52	2.05	105.0	56	3.70	2.60	48.3	33.9	51.7
Vacuum residue	> 480	0.9214	0.40	9.57	101.18	42	-	-	-	-	-

* K_o, Global number of cycles in the molecule

* K_a, Aromatic number of cycles in the molecule

* K_n, Naphthenic number of cycles in the molecule

* C_o, Carbon content in global structure in the molecule

* C_a, Carbon content in aromatic structure in the molecule

* C_n, Carbon content in naphthenic structure in the molecule

To study the properties of different components of the fractions and their involvement as load, these extracts had been subjected to vacuum distillation from which narrow fractions were isolated narrow fractions.

The curves characterizing the change of physico-chemical properties of the fractions isolated according of the extract are shown in fig.4a-4d.

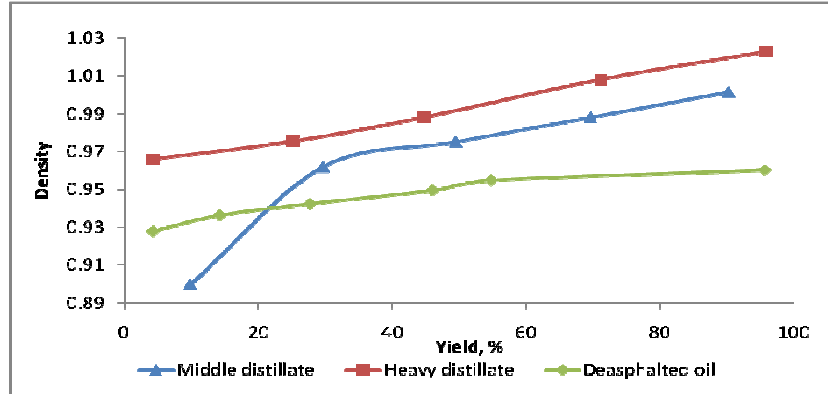


Fig. 4a. Curves characterizing the density for the 3 distillates

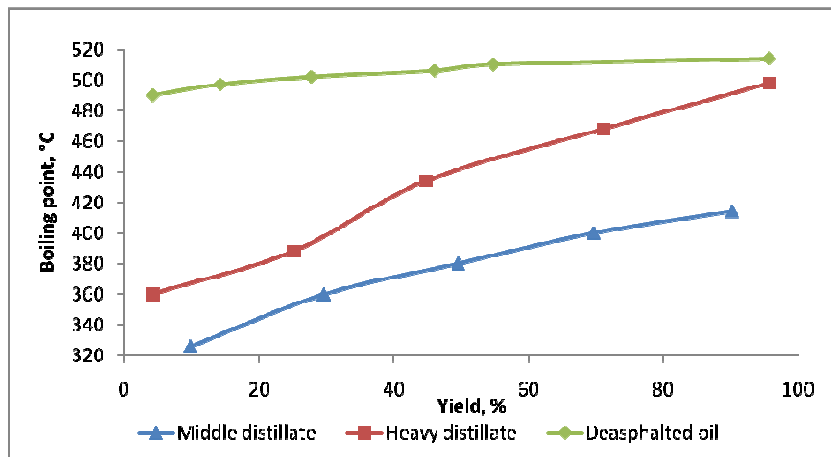


Fig. 4b. Curves characterizing the boiling temperature for the 3 distillates

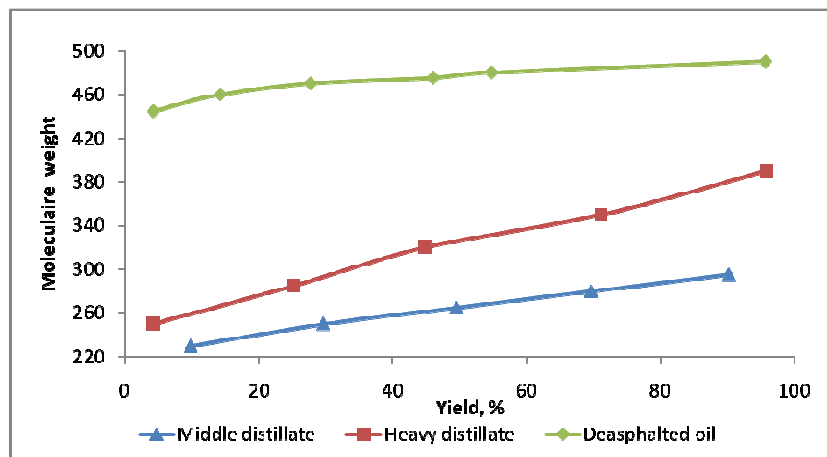


Fig. 4c. Curves characterizing the molecular weight for the 3 distillates

Physico-chemical characteristics of the extracts obtained by selective purification furfural distillate oil

Table 3

Products	Property	Yield % wt	Density d_4^{20}	Refractive Index n_D^{20}	Boiling point °C	molecular weight M	Sulphur content % Wt	Carbon Conradson % Wt	Composition of structural group							Coef. Arom A= K _o C _a	Correl Index CI	Rapport H/C
									Number of cycles			Carbon content, % Wt						
									K _o	K _a	K _n	C _o	C _a	C _p	C _n			
Middle distillate extract vacuum purified by furfural		100	0.9658	1.5544	380	265	0.56	0.14	2.85	1.95	1.90	77.6	46.2	32.4	21.4	132	75	1.32
Fraction	IBP- 350°C	19.6	0.8996	1.5067	326	230	0.37	-	1.95	1.20	0.90	57.7	35.5	42.3	22.2	69	50	1.48
Fraction	350 -370°C	19.8	0.9618	1.5496	360	250	0.48	-	2.75	1.80	0.98	69.5	45.5	30.5	24.0	125	76	1.32
Fraction	370 - 390°C	19.9	0.9751	1.5600	380	265	0.56	-	3.00	2.00	0.99	70.6	47.1	29.4	23.5	141	79	1.30
Fraction	390 - 412°C	20.1	0.9880	1.5680	400	280	0.63	-	3.40	2.20	1.20	74.3	48.1	25.7	26.2	163	84	1.26
Fraction	412 – EBP	20.6	1.0014	1.5782	414	295	0.71	2.04	3.80	2.40	1.40	77.2	48.8	22.8	28.4	185	89	1.24
Heavy distillate extract vacuum purified by furfural		100	0.9973	1.5748	410	330	0.67	1.43	3.85	2.45	1.55	70.4	44.8	29.6	25.6	173	83	1.30
Fraction	IBP - 373°C	8.4	0.9660	1.5502	360	250	0.48	-	2.70	1.70	0.98	67.6	42.5	32.4	25.1	115	75	1.36
Fraction	373 - 423°C	21.0	0.9754	1.5607	388	285	0.56	0.17	3.30	2.05	1.2	71.3	44.3	28.7	27.0	146	78	1.30
Fraction	423 - 453°C	19.6	0.9881	1.5686	434	320	0.63	-	3.80	2.40	1.3	71.8	45.3	28.2	26.5	172	80	1.28
Fraction	453 - 483°C	26.3	1.0080	1.5882	468	350	0.72	1.73	4.20	2.70	1.4	71.8	46.1	28.2	25.7	194	87	1.26
Fraction	483 - EBP	24.7	1.0227	1.5928	498	390	0.79	6.68	4.80	3.60	-	72.7	46.9	27.3	25.8	225	91	1.24
Deasphalted oil extracts vacuum purified by furfural		100	0.9525	1.5482	510	475	0.52	2.05	3.70	2.60	3.10	48.3	33.9	51.7	14.4	125	56	1.48
Fraction	IBP- 496°C	8.6	0.9279	1.5266	490	445	0.30	0.65	3.30	2.00	1.20	46.4	28.6	53.6	18.4	80	48	1.56
Fraction	496 - 499°C	10.0	0.9364	1.5324	497	460	0.36	-	3.50	2.20	1.15	47.2	29.6	52.8	17.6	105	50	1.54
Fraction	499 -504°C	13.5	0.9424	1.5372	502	470	0.40	-	3.55	2.30	1.10	47.5	30.1	52.5	17.4	107	52	1.52
Fraction	504 -508°C	18.3	0.9495	1.5452	506	475	0.48	-	3.70	2.60	0.99	47.9	33.6	52.1	14.3	124	56	1.50
Fraction	508 -510°C	8.7	0.9548	1.5512	510	480	0.58	-	3.80	2.80	0.98	48.4	35.6	51.6	12.8	135	58	1.48
Fraction	510 – EBP	40.9	0.9602	1.5557	514	490	0.71	3.13	3.90	3.00	0.97	48.5	37.3	51.5	11.2	145	60	1.46

* K_o, Global number of cycles in the molecule* K_a, Aromatic number of cycles in the molecule* K_n, Naphthenic number of cycles in the molecule* C_o, Global content carbon in the molecule* C_a, Aromatic content carbon in the molecule* C_p, Paraffinic content carbon in the molecule* C_n, Naphthenic content carbon in the molecule

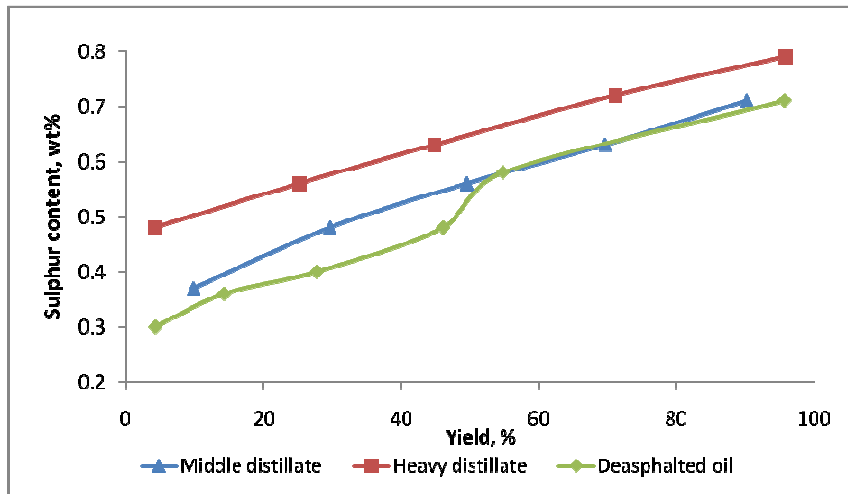


Fig. 4d. Curves characterizing the sulphur content for the 3 distillates

The curves characterize the structural composition of the group according to the average boiling temperature of these fractions are shown in Fig. 5-7. Note here that the structural composition of the group was established by GL method Guiliazeddinov [31].

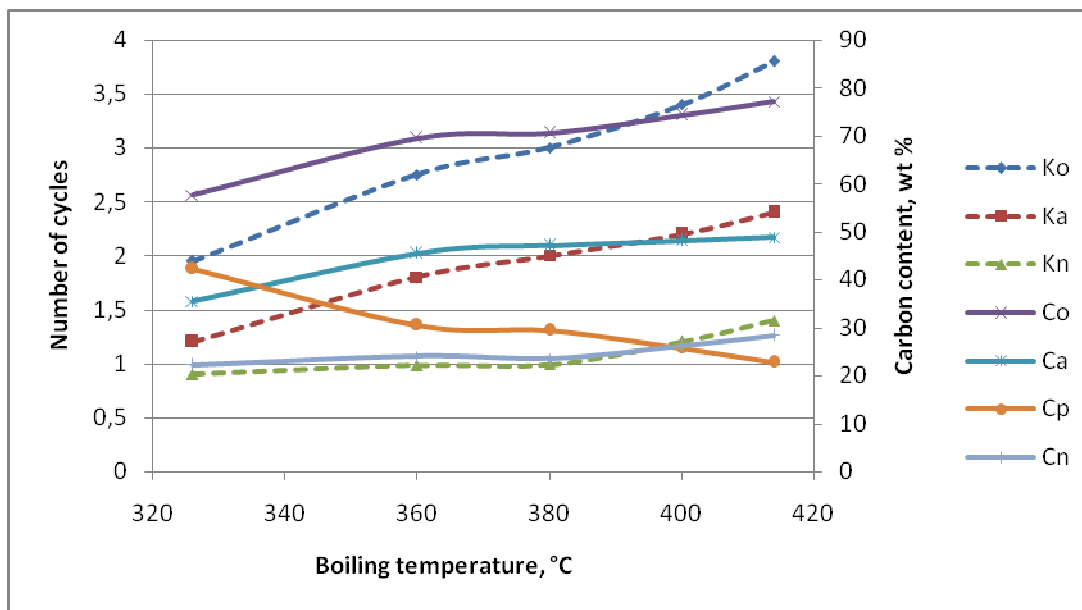


Fig. 5. Relationship between the structural composition of the narrow fractions group of the extract of middle distillate vacuum according to the boiling point: K_o , K_a , K_n – number of global, aromatic and naphthenic cycles in the molecule; C_o , C_a , C_p , C_n – carbon content in global; aromatic, paraffinic and naphthenic structures in the molecule

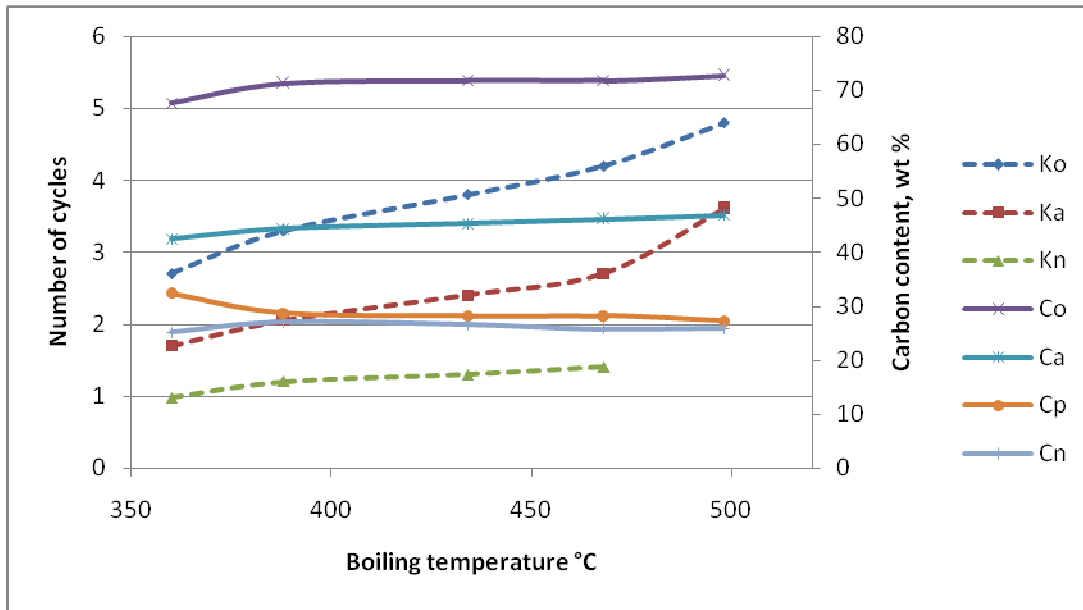


Fig. 6. Relationship between the structural composition of the group of narrow fractions of the extract of heavy distillate vacuum according to the boiling point: K_o , K_a , K_n – number of global, aromatic and naphthenic cycles in the molecule; C_o , C_a , C_p , C_n – carbon content in global, aromatic, paraffinic and naphthenic structures in the molecule

It should be noted that the carbon content in the paraffinic structures varies slightly, particularly for the de-asphalted distillate extracts maintaining a high level over (50%) fig.7 which makes this product of little use as FCC feedstock taking into account the composition of the heavy fraction

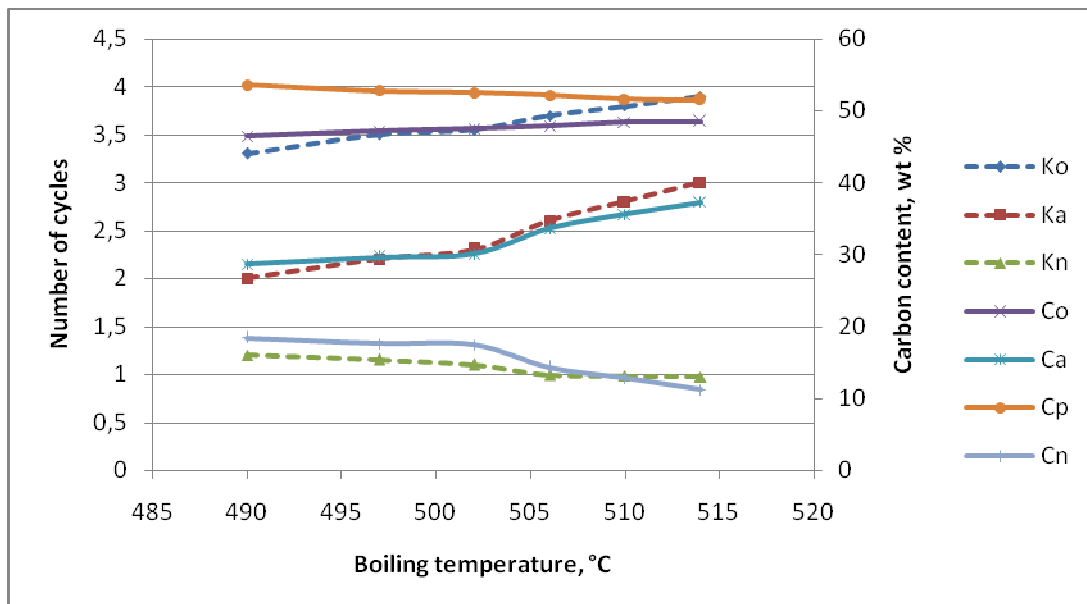


Fig.7 Relationship between the structural composition of the group of narrow fractions of the deasphalted oil extracts (vacuum residue) according to the boiling point: K_o , K_a , K_n – number of global, aromatic and naphthenic cycles in the molecule; C_o , C_a , C_p , C_n – carbon content in global, aromatic, paraffinic and naphthenic structures

Changes in the degree of aromaticity of the extracts according to the temperature are shown in fig. 8-10.

From these data it is advisable to say that with a rise in the average boiling temperature of the extracts, we observe a continuous decrease of the carbon content in the paraffinic structures and at the same time an increase of the carbon content in the cyclic structures. This increase in carbon in the cyclic structures is mainly due to aromatic hydrocarbons.

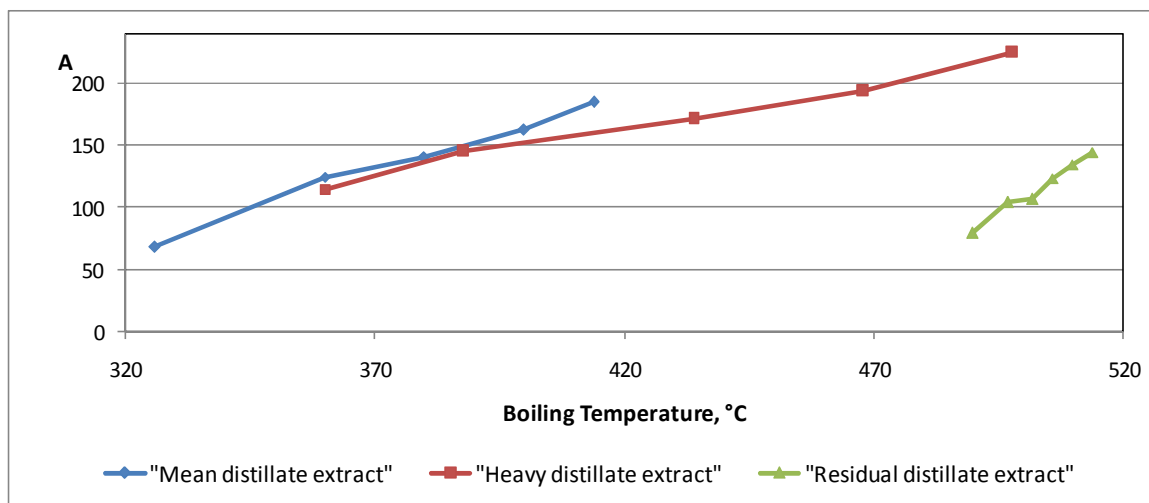


Fig.8 Variation of the extracts aromaticity according to the average boiling temperature:
A-coefficient of aromaticity

Based on the fractional composition, the distribution of carbon in structures is accompanied by a simultaneous change of the cyclization of the average molecule table 3.

With the increase in the average temperature of the middle vacuum distillate extract, the total number of cycles increases from 1.95 to 3.80, which occurred primarily because of the growth in the number of naphthenic cycles (0.9 to 1.4), while the growth in the number of aromatic cycles does not exceed 2.40

Similar scheme was observed with heavy vacuum distillate extract. In the contrary, the extract of the purification of the residual deasphalting, the number of naphthenic cycle decreases from 1.20 to 0.97, but the cross number of aromatic cycle is equal to 3.0.

Note that the carbon content in paraffinic structures change slightly especially for the extract of deasphalting that keeps its content at a high level above 50%, which makes the use of this product as inappropriate burden for this type of method

Moreover, with the rise of the boiling temperature of 326 ° C to 414°C increases the coefficient of aromaticity of the middle vacuum distillate extract from 69 to 185 Fig.8. It is the same for the index of correlation increases from 50 to 89 Fig.9. But the H / C ratio decreases in the same direction from 1.48 to 1.24 Fig.10.

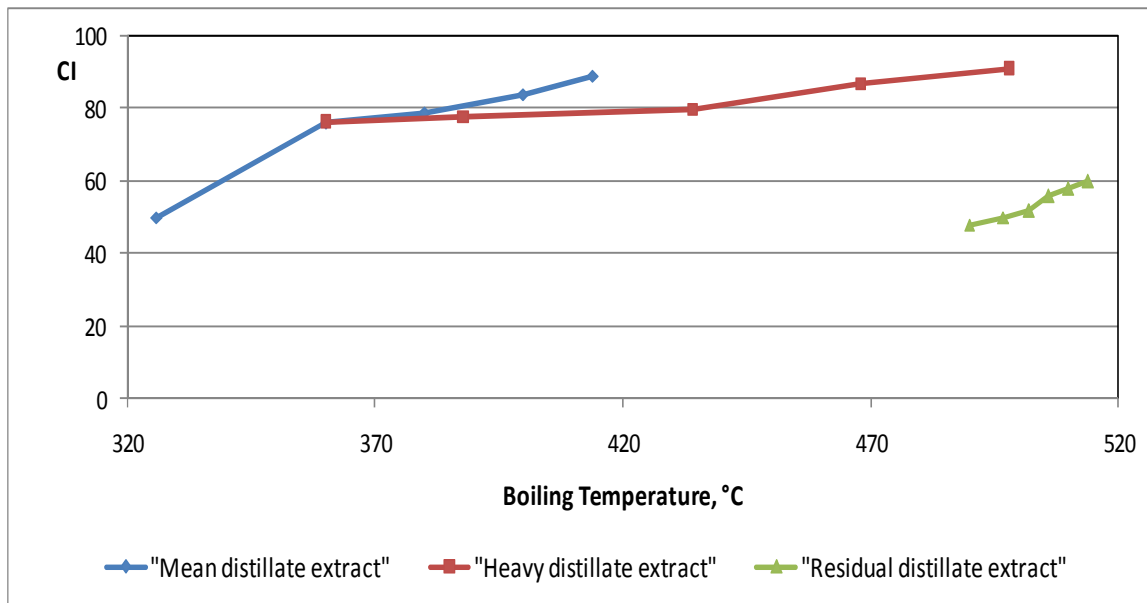


Fig.9. Variation of the extracts aromaticity according to the average boiling temperature from: CI- correlation index

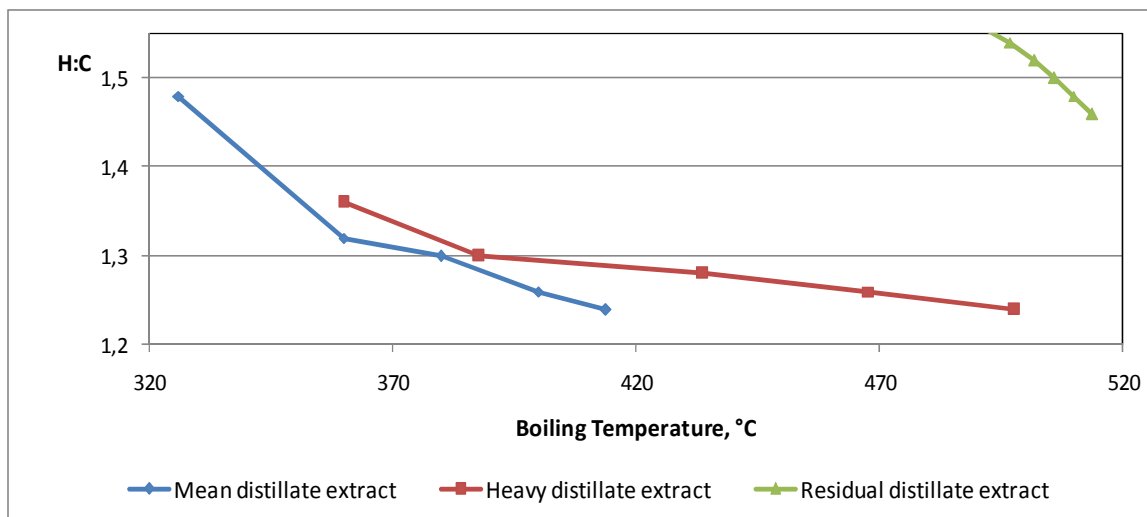


Fig.10. Variation of the extracts aromaticity according to the average boiling temperature from: H:C - ratio of hydrogen atom number to that of carbon atom.

It is true, that clearly notice an increase in the sulfur content from 0.37 to 0.71% wt and the content of coke up to 2% wt for middle vacuum distillate extract. Similar scheme was observed for all the fractions table 3.

The analysis results narrow fractions allow us to draw definitive conclusions about their usefulness as a raw material for the charges of the FCC

The comparison of the aromaticity of narrow fractions of the three types of load shows that fig.8 :
 - DAO residual fractions as raw material for the FCC, is inopportune because of their low aromaticity.
 - The same can be noted in respect of the top fraction (PI -350 °C) of the extract of middle vacuum distillate and the final fraction of the extract of heavy vacuum distillat (480°C -PF) could not be used as FCC feedstock; the first of these characteristics is the low aromaticity (correlation index equal 50), the second is its Conradson index which is 6.68% wt and its introduction into the feed leads to the formation of carbon deposits in the final product table 3.

The intermediate fraction of extracts of middle boiling in the range 350-480°C can be used as raw material for FCC

In light of what has been said, it is evident that the preparation and the use of extracts individually as raw materials is inappropriate

So it is preferable to prepare an industrial material balance by mixing medium extracts and heavy vacuum distillates proportionally in accordance with the selective purification installation's efficiencies of oils with furfural.

Then the mixture undergoes a vacuum distillation which removes the light top fraction, distilling up to 350°C and the heavy portion greater than 480°C. As appears from these data (Table 4), the material balance of the mixture has the following essential values: IC = 81, A = 169.

By comparing the material balance of the mixture of extracts of the vacuum medium and heavy distillates fraction 350-480°C (Table 4) shows that the vacuum distillation can improve some properties of the fraction into question particularly Conradson index which drop from 1.36 to 0.37% wt, the sulfur content is reduced from 0.62 to 0.55% wt, and a content allowed to Conradson index equal to 0.37% wt and a ratio of H/C=1.34. There was a slight decrease in the average boiling point and viscosity. (Table 4).

Physicochemical properties of the mixture of medium and heavy vacuum distillates extracts

Table 4

Properties	Mixture balance of the extracts of medium and heavy vacuum distillates	Fraction 350-480 °C
density d_4^{20}	0.984	0.9745
Refractive index	1.5676	1.5548
Boiling point °C	410	400
Molecular weight M	315	310
Sulphur content % Wt	0.62	0.55
Kinematic Viscosity V_{50} , mm ² /s	324	240
Carbon Conradson % Wt	1.36	0.37
Ratio of atoms H/C	1.33	1.34
Composition of structural group		
Number of cycles		
Total, K_o	3.7	3.6
Aromatics K_a	2.4	2.1
Carbon content dans la structure, % Wt		
Total C_o	70.5	71
Paraffinic, C_p	29.5	29
Naphthenic C_n	25	31
Aromatic C_a	46	40
Coefficient d'aromaticity $A=K_oC_a$	169	145
Correlation Index CI	81	77

An insignificant decrease in the correlation index (4 points) has no great importance, since the mixture is supposed to be used as a component in the composition of the charge with the residue of the catalytic cracking refinery Adrar the vacuum residue of the Arzew refinery which we will discuss later. Thus, at the basis of these analyzes and the results obtained, the prepared mixtures may be recommended as a feedstock for FCC processes

3.3. Study of heavy distillate mixture of catalytic cracking in Adrar refinery and vacuum residua in Arzew refinery.

In addition to aromatic extracts from oil manufacturing plants in Arzew refinery, the residua (heavy distillate) of catalytic cracking of Adrar refinery and the vacuum residua of Arzew refinery have been also studied as components of the FCC feedstock. All these products are unfortunately less valued; they are used as fuel in refineries for power production instead.

SARA analysis (saturates, aromatics, resins, asphaltenes) was performed on the residua or (heavy distillate) of catalytic cracking of Adrar refinery and the vacuum residua of Arzew refinery. It should be noted that asphaltenes were removed by solvent because of their nuisance on the catalysts and the chromatographic separation column; in what follows, it was decided that the SAR because their presence leads to their condensation and hence the creation of heavy products.

Table 5 presents some physicochemical properties of the heavy distillate catalytic cracking of Adrar refinery and the residue vacuum Arzew refinery.

Physicochemical properties of the heavy distillate catalytic cracking of Adrar refinery and the residue vacuum Arzew refinery. table 5

Properties	Heavy distillate FCC (Adrar)	Vacuum residue (Arzew)
density d_4^{20}	0.9218	0.9407
Boiling point °C	478	510
Pour Point °C	+27	+32
Flash Point °C	72	290
Sulphur Content ppm	1300	4000
Carbon Conradson (% Wt)	3.2	7.0
Molecular weight M	-	480
Characterization factor (Kuop)	11.18	12.22
Analyse SARA		
% Saturates	23.336	48.739
% Aromatics	74.066	41.025
% Resins	1.975	9.701
% Asphaltenes	0.623	0.535

Since the residua or (heavy distillate) of catalytic cracking of Adrar refinery and the vacuum residua of Arzew refinery are residua that having a large percentage of aromatics, we can compound them and prepare a material balance proportionally mixing the two residua table 6.

Physicochemical properties of the mixture of the heavy distillate catalytic cracking of Adrar refinery and the residue vacuum Arzew refinery. table 6

Properties	Mixture of the Heavy Distillate FCC (Adrar) And Vacuum Residue (Arzew) 50 : 50
Boiling point °C	494
Density d_4^{20}	0.9311
Kinematic Viscosity à 100°C, mm ² /s	14.99
Flash Point °C	181
Sulphur Content ppm	0.26
Carbon Conradson (% Wt)	4.66
Molecular weight M	417
Characterization factor (Kuop)	11.73
Analyse SARA	
% saturés	36.037
% aromatiques	57.546
% Résines	5.513
% asphaltènes	0.579

3.4. Implementation of appropriate process for the valorization of prepared loads

Since the objective of our work is to optimize these heavy cuts obtained by compounding different proportionalities between different sections mentioned above, we are limited to the valorisation of these products by studying the implementation of the catalytic cracking process. The latter is currently the most suitable conversion process and most important in terms of quantities of products with high market value on one hand and the only one that exists in Algeria on the other hand.

The feed used in the catalytic cracking process is a complex mixture of Adrar Heavy Mixture Distillate FCC and Vacuum Residua Arzew plus the extract fraction 350-480°C see table 7. The tests were conducted on a laboratory plant. The operating conditions were maintained for all feedstocks and are respectfully: P=1.2 atm T°C=480°C and WWH=1.33. The values of compounding are shown in table 7

In the presence of catalyst, at high temperature (450-550°C) and at atmospheric pressure, we break larger hydrocarbon molecules to smaller ones having a high octane number. The industrial process often used is the "FCC" or "Fluid Catalytic Cracking".

It is based on the use of a fluid bed catalyst. The catalyst used was a commercial catalyst of the series zeolites of existing on the national market under the name of NaY CBV100, a size of about 50 micrometers, is suspended in the feed, which, after preheating, is injected into the reactor in gaseous form Fig.4

After passage of feedstock into the reactor, all the products pass into the fractioning plant and at the outlet following products can be collected table 8.

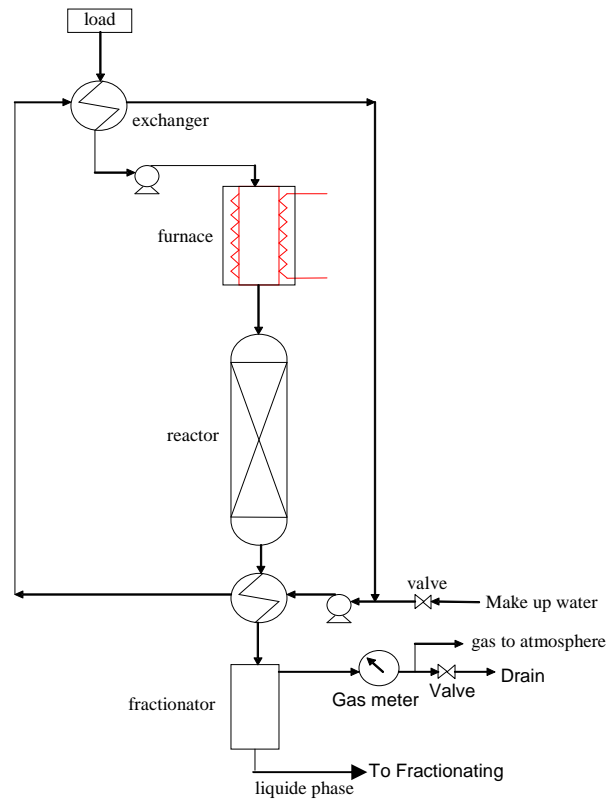


Fig.4. Laboratory plant Catalytic Cracking

Charges of potential catalytic cracking

Table 7

Properties	Extract 100%	Mixture Adrar and Arzew + Extract 50/50	Mixture Adrar and Arzew + Extract 60/40	Mixture Adrar and Arzew + Extract 80/20	Mixture Adrar and Arzew + Extract 90/10	Extract+Mixture Adrar and Arzew 50/50	Extract+Mixture Adrar and Arzew 60/40.	Extract+Mixture Adrar and Arzew 80/20	Extract+Mixture Adrar and Arzew 90/10	Mixture Adrar and Arzew 100%
Boiling point (°C)	400	447	456	475	484	447	456,4	475.2	484.6	494
Density d_4^{20}	0.9745	0.9524	0.9479	0.9394	0.9353	0.9524	0.9480	0.9395	0.9353	0.9311
Kinematic Viscosity à 100°C, mm ² /s	240 à (50°C)	18.5	16.40	15.10	14.80	18.5				14.99
Flash Point°C	165	173	171	168	166	173				181
Sulphur Content (ppm)	0.55									0.26
Carbon Conradson (%Wt)	0.37	0.39	0.42	0.47	0.49	0.39				12.7
Molecular weight M	310	363.5	374.2	395.6	406.3	363.5	352.8	331.4	320.7	417
Characterization factor (Kuop)	10.94	11.45	11.55	11.75	11.85	11.45	11.56	11.78	11.88	11.73
Analyse SARA										
% Saturates	27.134	31.5855	30.6952	28.9146	28.0243	31.5855	30.6952	28.9146	28.0243	36.037
% Aromatics	70.488	64.0170	65.3112	67.8996	69.1938	64.0170	65.3112	67.8996	69.1938	57.546
% Resins	1.578	3.5455	3.1732	2.3650	1.9715	3.5455	3.1520	2.365	1.9715	5.513
% Asphaltenes	0.875	0.7270	0.7566	0.8158	0.8454	0.7270	0.7566	0.8158	0.8454	0.579

4. Results and discussions

The results obtained are shown in table 8 and the histogram fig .5. After these results, we can see that the feed mixture composed of Arzew vacuum residua and catalytic cracking residua of Adrar of paraffinic tendency provides maximum gasoline (52%) and little coke.

This can be explained by the fact that the paraffin cracking provides paraffin and olefins of lower molecular weight. The coke is the result of cracking as dehydrocyclization form followed by polycondensation. But these reactions are not the majority.

As the paraffinicity of the feed remains and aromaticity increases, there is a decrease in gasoline yield and an increase in the gas yield. This can be explained by the fact that aromatics of the feed are alkylated and the cracking reaction releases these radicals which transformed into gas given their low molecular weight. The coke yield increased to the feed n°7 due dehydrocyclization reactions followed by polycondensation reactions. The gas yield increases for feeds 8 and 9 and the gasoline yield decreases slightly; these two products are formed primarily by reactions of aromatic désalkylation. The released nuclei can condense to form coke. This explains the low yield of this product.

Feed n°10 is primarily aromatic. Gasoline yield is relatively low, but it has a good quality. The coke yield is relatively low due to polycondensation reactions that are not in the majority, conversely the yield of diesel and slurry is high. These consist of mainly dealkylated aromatics, paraffin and olefins of long chain.

Finished products yield in%

Table n° 8

N°	Charge	gas	gasoline	Gas-oil	slurry	coke
1	Mixture Adrar and Arzew 100%	7.50	52.00	18.00	17.20	5.30
2	Extract+Mixture Adrar and Arzew 90/10	10.01	50.00	17.00	17.62	5.37
3	Extract+Mixture Adrar and Arzew 80/20	10.27	45.00	18.52	17.00	9.21
4	Extract+Mixture Adrar and Arzew 60/40	11.02	40.50	19.60	16.50	12.38
5	Extract+Mixture Adrar and Arzew 50/50	12.50	38.50	20.02	16.00	12.98
6	Mixture Adrar and Arzew + Extrait 90/10	13.27	36.0	21.80	15.80	13.13
7	Mixture Adrar and Arzew + Extract 80/20	14.26	35.00	22.25	14.75	13.74
8	Mixture Adrar and Arzew + Extrait 60/40	15.01	35.50	23.14	17.00	9.35
9	Mixture Adrar and Arzew + Extract 50/50	15.42	31.50	24.00	18.50	10.58
10	Extract 100%	12.00	30.00	28.00	23.07	6.93

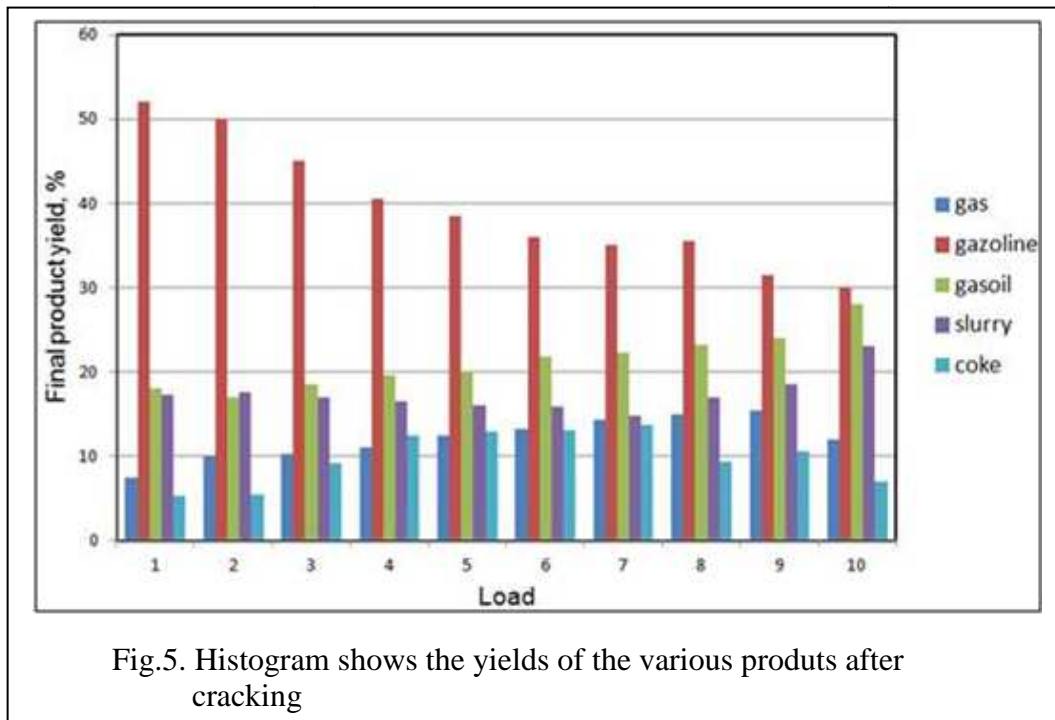


Fig.5. Histogram shows the yields of the various products after cracking

5. Conclusion

The atmospheric and vacuum residue, catalytic cracking residue and extracts of aromatic oil fractions are used only for the preparation of fuels. Alone or in mixture, they are added to diesel fuel to improve some properties such as viscosity and vapor pressure.

But due to their chemical composition, highly paraffinic for the residua and aromatic for the extracts, it was possible to make their use as feedstock in the catalytic process. To do this, these products are analyzed individually then mixtures in different proportions were carried on. This allowed us to obtain feedstocks which are quite interesting for valuation in the catalytic process.

The implementation of the experiment was done in laboratory with a commercial catalyst. We could obtain gasoline fractions of aromatic composition well pronounced and high octane number, gas oil features comply with standards and two fractions of propane-propylene/ butane-butylene interesting in petrochemicals. All these products are obtained with significant yield. On the basis of these results, these tests can be applied in a pilot plant before transferring them into an industrial plant facility.

To raise more yields, we suggest the recycling of heavy residue obtained in the fractioning section of the cracking products. This residue or slurry is highly aromatic, and can therefore improve the quality of gasoline by increasing its octane number.

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Nomenclature

A	Coefficient of Aromaticit
CI-	Correlation index
CS ₂	Carbon disulphide
H/C	Ratio of Hydrogen atom number to that carbon atom
C _o	Global content carbon in the molecule
C _a	Aromatic content carbon in the molecule
C _p	Paraffinic content carbon in the molecule
C _n	Naphtenic content carbon in the molecule
K _{UOP}	Characterization factor
K _o	Global number of cycles in the molecule
K _a	Aromatic number of cycles in the molecule
K _n	Naphtenic number of cycles in the molecule
PPM	Parts per million
P	Pressure
n_D^{20}	Refraction index
Ni	Nickel
T	Temperature
V	Vanadium
WWH	Space velocity

Abbreviation

CanMet,	Canada Research Centre for Mineral and Energy Technology
CCR	Conradson carbon residue
DAO	Deasphaltisat Oil
FW	Foster Wheeler
FCC	Fluid Catalytic Cracking
HCO	Heavy cycle oil
HDH	Hydrocracking distillation hydrotreating
HDH Plus	Slurry Hydrocraker (HDH Plus), HDHPLUS/SHP technology (the Puerto La Cruz refinery)
Hyvahl-F	IFP's trade mark for a fixed bed reactor hy-drotreating process
Hyvahl-M	IFP's trade mark for a moving bed reactor hydrotreating process
Hyvahl-S	IFP's trade mark for a swing reactor hydro-treating process IFP Institut Francais du Petrole
H-Oil	H-Oil _{RC} (RC stands for Resid Cracking) process uses ebullated-bed hydrocracking technology
LC Fining	Hydrocracks residuum to high-quality fuel oils and transportation fuels
LCO	Light Cycle Oil (gazole from cracking catalytic)
PdVSA	Petróleos de Venezuela SA (Petroleum of Venezuela)
RFCC -	Residue Fluidized Catalytic Cracking
SARA	Saturetes, Aromatics, Resins, Asphaltenes
HYCON Shell's	Trade mark for a hydroconversion process<
Slurry	Clarified catalytically cracked oil
TBP	True boiling point
TLC-FID	Thin Layer Chromatography with Flame Ionization Detection
UOP	Universal Oil Products

Appendix

List of ASTM norms used in the laboratory

NN	Properties	Norms ASTM
01	Distillation Range°C	ASTM D 86, D 1160
02	Density d_4^{20}	ASTM D 1298, D 4052
03	Sulphur Content % Wt	ASTM D 2774
04	Carbon Conradson % Wt	ASTM 189-65
05	Kinematic Viscosit V_{100} mm ² /s	ASTM 445, D88
06	Corrélation Index CI	$\frac{48640}{T^{\circ}K} + 473.7 * spgr - 456.8$
07	Flash Point°C	ASTM D 56
08	Pour point °C	ASTM D 97
09	Analyse SARA	Iatroscan TLC-FID - Thin Layer Chromatography with Flame Ionization Detection
11	Coefficient of aromaticity	$A=K_o \cdot C_a$