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STUDY OF THE THERMAL CRACKING DURING THE VACUUM DISTILLATION OF ATMOSPHERIC RESIDUE OF CRUDE OIL

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Abstract: This article concerns the study of the thermal cracking as undesirable phenomenon in the vacuum distillation of atmospheric residue of crude oil. In this point, we have sought to identify and characterize the effect of the increase in the temperature of vacuum distillation on the separation and the modification of the constituents of atmospheric residue of crude oil whose origin is Arabian Light. This study has been carried out by several techniques of analysis such as the density (ASTM D4052), distillation (ASTM D1160), determination of heavy metals nickel and vanadium (IFP9422), dosing of Conradson Carbon (ASTM D189), dosing of asphaltenes (ASTM D2549) and dosage of PCI (polycyclic aromatics) (ASTM D 5186). The results showed a clear idea on the decomposition of the atmospheric residue and their influence on the performance of the vacuum distillation unit.

Keywords: *barometric diesel, coker, Conradson carbon, rupture β-scission, vacuum gas oil*

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INTRODUCTION

The petroleum refining begins at first by atmospheric distillation to separate crude oil into different groups of hydrocarbons. In term of quality and quantity, the products obtained directly depend on the quality of the processed crude. The yields of these valuable products do not exceed 60 % in most of crudes oil feedstock [1 − 4]. Moreover, to increase yields of valuable products, refineries conduct vacuum distillation that allows a re-distillation of the heavy part from atmospheric distillation to obtain high-value products [5, 6].

Distillation is a process, which comprises separating hydrocarbon fractions contained in the crude oil. The principle of this fractionation is based on the difference in boiling temperature of each compound contained in the crude oil feedstock [1 − 7].

In the atmospheric distillation, or the operation carried out at atmospheric pressure, heavy products that exist at the bottom of the column practically cannot be separated without increasing the distillation temperature. Indeed, at a temperature of 360 °C and at atmospheric pressure, crude oil begins to be degraded because of the phenomenon of thermal cracking. This phenomenon impacts the quality and quantity of the distillation products obtained.

In order to separate these products without changing their chemical structures in range of temperatures from 390 to 400 °C, there is a method of vacuum distillation where the pressure is reduced up to 1.33×10^3 and 2×10^3 Pa [8].

Thermal cracking is the oldest process in the petroleum refining, based on the principle of decomposition or thermal conversion of heavy fractions into light hydrocarbon fractions [9]. Thus, it is common in some refining operations such as Coker and Visbreaker technologies whose facilities are appropriate for these kinds of operations. For vacuum distillation too, thermal cracking is a constraint for increasing the distillation temperature, which aims to perform an optimal different compounds structures, also to avoid undesirable consequences such as:

- Production of harmful products such as coke and highly corrosive incondensable gases.
- Decrease the heat transfer performance in the heat exchangers and the furnace causing clogging problem of product transfer lines.
- Higher cost for maintenance and cleaning of filters, pumps and heat exchangers.
- Moving heavy fractions and vacuum residue metals to the products intended to catalytic units, representing a limitation of the catalytic activity of these units by catalyst poisoning by these metals.

In this work, we proceed to study the thermal cracking phenomenon of the vacuum distillation unit in a real operating system in a continuous load of 250000 kg·h⁻¹.

The thermal cracking in the vacuum distillation of atmospheric residue, a number of analytical methods have been applied to collect and characterize samples from each vacuum distillation. Thus, different analyses have been carried out such as density (ASTM D4052), distillation (ASTM D1160), the determination of heavy metals such as nickel and vanadium (IFP9422), carbon dosage Conradson (ASTM D189), the dosage of asphaltenes (ASTM D2549) and the determination of polycyclic aromatic compounds PCI (ASTM D 5186).

MATERIALS AND METHODS

Description of process

This study focuses on thermal cracking as undesirable phenomenon in the vacuum distillation of atmospheric residue from a crude oil. The plant concerned with this work has a capacity of 250000 kg·h^{-1}, with a feed of originated from Arabian light oil.

As a first step in refining processes, the crude oil is subjected to atmospheric distillation, where light and heavy parts of the oil are separated based on their boiling point. Then the heavy part, which called the atmospheric residue, is used as feed in the vacuum distillation. In this process the feed is first pumped through a furnace (Figure 1) mixed with a medium vapor pressure to accelerate the flow of the mixture in the furnace tubes. The mixture is partially vaporized and reaches a temperature level called temperature of transfers (this temperature is the key parameter to adjustment operations in these tests). The vaporization continues through the furnace tubing until it reaches the distillation column at 1.33×10^4 Pa absolute pressure. The vacuum (1.6×10^3 Pa) condition is created and controlled by different ejector of medium pressure steam in the top of the column. In the bottom of the column, the superheated water vapor is also introduced in the feed area of the mixture to decrease the partial pressure of hydrocarbons.
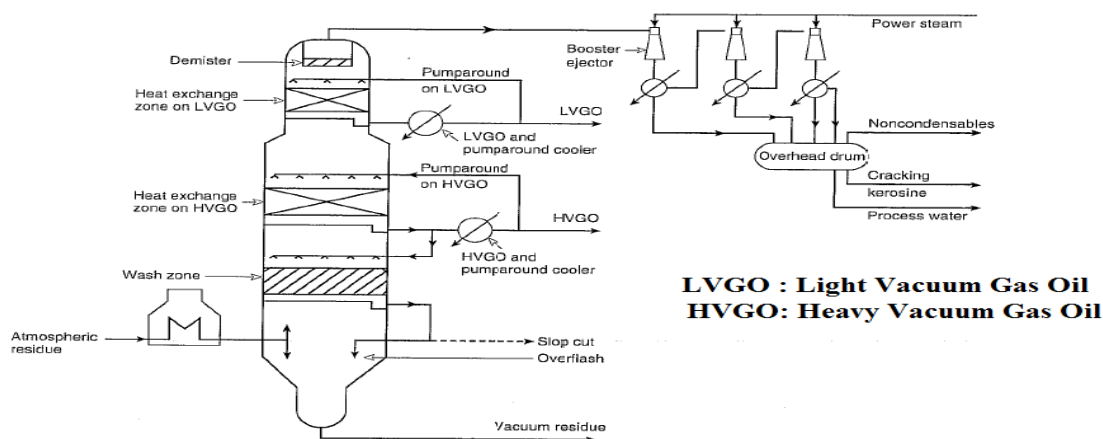

Figure 1. Flow diagram of a dry vacuum distillation unit [9]

The sampling procedure

The sampling was made after 6 hours to 8 hours of stability of the unit (in terms of trays temperatures, column vacuum pressure, product yields and reflux flow rates) following a change in furnace outlet temperature (temperature of transfers). Samples intended for the physico-chemical analysis were collected in metal bottles of 1 Liter following the standard (ASTM D4057).

In order to characterize all samples and for a better understanding of the vacuum cracking phenomenon, the following analyses have been carried out like:
- The distillation of slices racked (ASTM) for LVGO (Light Vacuum Gas Oil), VGO (Vacuum Gas Oil) and barometric diesel.

- The concentrations of heavy metals nickel and vanadium for VGO.
- Concentration in carbon Conradson paved and for VGO and HVGO (Heavy Vacuum Gas Oil).
- The density for RSV, VGO and LVGO.
- Gas chromatography for the incondensable gases.

RESULTS

The experimental results of each product in vacuum distillation are presented in the first place the one separate to the other.

Vacuum residue (RSV)

The vacuum residuals (RSV) are derived from the vacuum distillation of atmospheric residue of crude oil tankers. Their normal boiling point, to P_{atm} is higher than 550 °C. They are enriched in metals and compounds of high molecular weights more than 25 carbon (C25). The RSV is a mixture of aromatic molecules and saturated compounds. They are associated to form a colloidal system whose stability depends on the characteristics of its compounds [10]. The temperature of vacuum distillation played a very important role in the depletion of RSV and in the characterization of quality of RSV, on the side viscosity and density as indicated in the Table 1.

Table 1. *Performance results and analysis of RSV according to the variation in the outlet furnace temperature*

RSV Temperature outlet the furnace [°C]	Yield in weight [%]	Density [kg·m⁻³]	Viscosity at 100 °C [m²·s⁻¹]	Viscosity at 50 °C [m²·s⁻¹]
380	52.8	1015	8.95×10^{-5}	1.231×10^{-4}
382	51.2	1020	9.48×10^{-5}	1.349×10^{-4}
384	49.2	1018	1.041×10^{-4}	1.415×10^{-4}
386	48	1022	1.079×10^{-4}	1.488×10^{-4}
388	46	1026	1.119×10^{-4}	1.632×10^{-4}
390	45.2	1026	1.208×10^{-4}	1.751×10^{-4}
392	45.2	1028	1.428×10^{-4}	2.079×10^{-4}
394	44	1030	1.522×10^{-4}	Does Not Flow*
396	41.6	1031	1.713×10^{-4}	Does Not Flow
398	38	1033	Does Not Flow	Does Not Flow
400	33.6	1034	Does Not Flow	Does Not Flow

* it is very viscous

Vacuum gas oil (VGO)

Vacuum gas oil is, by definition, the distillable fraction of atmospheric residue (RA) with a distillation range between 375 and 615 °C. In other words, it is the mixture of heavy and medium vacuum gas oil.
The Table 2 represents the results of the analysis and performance of VGO in function of the furnace temperature.

Table 2. *Performance results and analysis of VGO according to the variation in the outlet furnace temperature*

VGO		380	382	384	386	388	390	392	394	396	398	400
VGO		**Temperature [°C]**										
Yield in weight [%]		38.4	39.2	40.8	41.6	43.6	44	44.2	44.5	46.3	48.3	50.5
Density [kg·m⁻³]		925.5	925.8	926.5	926.5	927	927.2	928	928.6	929	929.5	930
A S T M D 1 1 6 0	**Initial boiling point**	312	310	312	312	315	316	317	320	320	322	324
	5 % V	369	369	368	370	370	372	377	377	376	377	377
	10 % V	372	370	385	385	388	389	388	390	394	393	395
	20 % V	410	412	415	415	415	416	418	420	422	423	425
	30 % V	430	430	435	435	438	442	444	446	447	449	447
	40 % V	451	452	455	450	457	457	456	454	458	460	459
	50 % V	462	466	466	470	473	472	476	475	476	480	478
	60 % V	488	490	491	492	490	494	496	496	499	500	502
	70 % V	510	510	515	515	515	516	517	517	519	518	521
	80 % V	528	528	528	528	530	532	534	534	536	533	538
	90 % V	550	552	555	550	557	557	557	561	562	560	566
	95 % V	570	576	578	578	576	578	579	580	584	588	588
	Final boiling point	615	616	619	621	622	622	625	627	628	636	634
	Residue [%]	2	1.6	2.1	1.9	2	2	2.2	1.8	1.7	2.1	2
Nickel [ppm]		0.4	0.6	0.8	1.2	1.5	2	2.2	2.3	2.2	2.4	3
Vanadium [ppm]		1.8	1.7	2.4	2.5	2.8	2.9	2.9	3.3	3.4	3.8	4.1
Conradson [% w]		0.75	0.75	0.83	0.82	0.84	0.88	0.92	0.95	1.02	1.1	1.23
Asphaltenes [ppm]		1065	1265	1320	1460	1665	1750	1985	2375	2660	3070	3150
PCI [ppm]		1670	1750	2075	2075	2150	2225	2415	2675	2945	3385	3275

Light vacuum gas oil (LVGO)

LVGO is the upper side stream outlet of the vacuum column. Its quality and quantity varies directly with the change of the temperature of transfers.
The Table 3 represents the results of the analysis and performance of LVGO in function of the outlet furnace temperature.

The hydrocarbons of cracking or barometric diesel

These are the hydrocarbons produced by cracking of the load within the tubes of the furnace. They are found in the head of the column along with the incondensable gases and the steam injected into the process. They have been separated in the barometric overhead drum. The Table 4 represents the results of the analysis and performance of barometric diesel in function of the outlet furnace temperature.

Table 3. *Performance results and analysis of LVGO according to the variation in the outlet furnace temperature*

LVGO		Temperature [°C]										
		380	**382**	**384**	**386**	**388**	**390**	**392**	**394**	**396**	**398**	**400**
Yield in weight [%]		7.6	8.8	8.8	9.1	9.2	9.3	9.5	10.1	11.1	12.2	13.3
Density [kg·m^{-3}]		888	889	889	890	890	892	892	892	893	893	893
A S T M D 1 1 6 0	**Initial boiling point**	255	254	258	263	267	267	270	273	279	283	286
	5 % V	265	265	267	266	269	272	276	277	279	278	283
	10 % V	275	287	288	290	292	295	297	299	304	306	310
	20 % V	288	288	293	295	300	302	305	305	309	313	320
	30 % V	295	297	300	304	304	306	308	314	323	327	333
	40 % V	298	301	304	309	314	315	312	319	334	335	339
	50 % V	305	308	312	316	320	319	318	321	334	343	345
	60 % V	310	311	314	325	328	330	333	336	337	345	349
	70 % V	315	319	321	327	330	334	338	340	345	350	355
	80 % V	330	334	336	340	342	343	348	353	360	361	367
	90 % V	345	350	355	363	363	365	368	373	373	377	381
	95 % V	354	358	361	370	373	375	375	381	386	391	396
	Final boiling point	370	374	377	382	383	382	385	388	393	396	>400
	Residue [%]	1.4	1.5	1.3	1.9	2.1	2	2.6	2.4	2.1	2.4	2.5

The incondensable gases

These compounds produced by thermal cracking are incondensable gases, a mixture of light hydrocarbons and gas, drawn by the vacuum system. They have to be treated in gas treatment plant prior to be used as fuel in refinery furnaces or burnt at the torch. The following table represents the results of the analysis and performance of *incondensable gases* in function of the outlet furnace temperature.

Table 4. *Performance results and analysis of barometric diesel fuel according to the variation in the outlet furnace temperature*

Barometric Diesel		Temperature [°C]										
		380	382	384	386	388	390	392	394	396	398	400
Yield in weight [%]		0.8	0.88	1	1.08	1.2	1.29	1.38	1.87	2.6	2.8	3.13
Density [kg·m⁻³]		790	791	792	793	793	794	794	794	794	794	794
A S T M D 1 1 6 0	Initial boiling point	102	10 3	105	109	109	110	110	112	112	114	116
	5 % V	114	115	117	116	120	121	119	117	121	120	123
	10 % V	125	128	128	131	133	136	134	132	135	132	136
	20 % V	132	131	135	139	144	150	152	153	155	150	153
	30 % V	159	160	160	160	163	164	165	167	166	160	163
	40 % V	166	166	170	175	177	178	176	172	177	174	172
	50 % V	178	176	180	183	186	189	187	185	183	181	185
	60 % V	191	190	190	193	198	201	202	200	201	203	202
	70 % V	202	200	203	208	210	215	214	213	213	210	214
	80 % V	238	231	238	235	240	236	236	232	233	230	234
	90 % V	243	247	247	246	250	256	256	254	254	260	258
	95 % V	257	260	261	262	266	276	277	276	275	280	278
	Final boiling point	262	263	263	271	274	278	279	282	280	283	283
	Residue [%]	1.3	1.4	1.2	1.5	1.4	1.7	2	1.9	1.8	2.1	2

Table 5. *Performance results and analysis of incondensable gases according to the variation in the outlet furnace temperature*

Incondensable gases	Temperature [°C]										
	380	382	384	386	388	390	392	394	396	398	400
Yield in weight [%]	0.31	0.42	0.58	0.68	0.8	1.06	1.21	1.76	2.08	2.23	2.58
H_2 % V	14.2	14.6	15	15.6	16.3	16.5	16.6	17.7	18.7	19.2	21
N_2 % V	2.84	2.87	3.1	3.3	3.4	3.9	3.1	3.6	2 ,83	3	3.2
C1 % V	26.2	26.3	29.2	29.5	30	30.4	28.4	28.4	30	30.4	32.5
C2 % V	15.3	15.8	14.2	14.5	14	14.6	13.9	13.9	14.2	13.9	14.6
C3 % V	13.2	13.8	12.3	12.7	12	12.5	12.9	12.5	12.8	11.8	13
iC4 % V	6.1	5.7	5.1	5.2	5	5.5	5	5.4	5.3	5	3
nC4 % V	6.3	6.9	6.3	6.3	6	6 .5	6.8	6.4	6.1	5.8	3.5
iC5 % V	4.3	4.3	4.1	3.9	3.8	4	3.3	3.1	3.2	2.5	2.5
nC5 % V	4.2	3.6	3.8	3.4	4	4.2	4	3.6	3.7	3.1	2.3
trans-2-butene % V	2.5	2.1	1.8	1.5	1.9	2.8	2.2	2.1	2.2	2.4	1
1-butene % V	2.2	1.4	1.9	1.3	1.6	1.5	1.1	1.2	1.4	1.4	0.9
O_2 % V	2.1	2	2.3	2.5	2	2.8	1.9	1.7	1.7	1.2	1.8
H_2S % V	0.46	0.56	0.55	0.56	0.53	0.6	0.62	0.65	0.7	0.73	0.78

DISCUSSION

In this study, we investigate the phenomenon of thermal cracking during vacuum distillation of atmospheric residue, in other words we investigate the influence of the change in the temperature of distillation vacuum on the quality and quantity of all products withdrawn laterally from the column of vacuum distillation of atmospheric residue. And therefore, to deduct the optimal temperature of distillation which gives us the rated maximum yields of the distillates to meet the requirements of the units in the downstream such as the minimum of RSV, incondensable gases and coke product. The strategy adopted is the following:

➢ Analyze all products is the result of the vacuum distillation in order to understand the impact of the change of the temperature on the vacuum distillation.
➢ Evaluate the phenomena in place during the temperature increase of vacuum distillation by keeping all other parameters fixed.

We have chosen to measure the general parameters commonly used for the evaluation of the quality of withdraw products (density and performance); and the specific parameters to products as a percentage of metals (vanadium and nickel), percentage of polycyclic aromatic PCI, Conradson carbon, viscosity to either 50 or 100 °C and the distillation ASTM D1160.

Vacuum residue

As regards the RSV, it has been measured that significant variations in yield, density (from 1015 to 1034 kg·m^{-3}) and viscosity occurs related to vacuum distillation temperature.

This variation of the viscosity is due mainly to the total exhaustion of atmospheric residue in the operation of vacuum distillation during the increase of the temperature of vacuum distillation up to 394 °C, or we observe that the product residue vacuum becomes very viscous, heavy and does not flow even at temperature of 50 °C. This can cause problems for plugging the flow lines and the beds in the trim as shown in Figure 2 below.

Figure 2. Filling of coke in a tube of oven and bed of trim

This situation could be explained by the reactions of rupture of the free radicals (*β*-session) [12 – 13] and the reactions of condensation of polyaromantic structures cyclical, which gives the formation of the vacuum residue very viscous and very heavy or where it begins at the same time formation of coke [14 – 17].

Vacuum gas oil

The VGO is the mixture of HVGO and MVGO (Medium vacuum gas oil). The results obtained show that the increase in the temperature of vacuum distillation to the effect of the redistribution of the cut point of atmospheric residue between the VGO represented by HVGO and MVGO. This redistribution of the slices appears clearly in the movement of cut points of VGO (initial point up to the final point of distillation) in parallel with the increase in the temperature of vacuum distillation. This influence directly on the performance of VGO, including the significant increase in detriment of performance of RSV, but at the same time it has a drawback on the quality of the VGO. This quality, which is contaminated with larger amounts of heavy metals such as nickel and vanadium, or cyclic polyaromatic compounds (PCI) and asphaltenes. These compositions could lead to catalysts poisoning in conversion units such as reformers when they exceed specifications [18, 19].

Light vacuum gas oil and barometric Diesel

As regards the LVGO and GB (the barometric diesel), we can say that these two products have also undergone a change of the composition and performance in parallel to the increase in the temperature of vacuum distillation. The analysis shows that the cut points of two products are experiencing a shift toward a significant increase, which presents a heavier product. This increase appears also in the increase of the density with temperature [20].

The incondensable gases

 As regards the incondensable gases, one finds that the quantity of incondensable gases produced in parallel with the increase in the temperature under the empty varies from 0.31 to 2.58 % of the total load processed. This variation of the quantity is characterized by a change in the composition of the incondensable gases. It is important to note that the higher the temperature of vacuum distillation increases, the more the amount of hydrogen, methane, ethane and propane increases in detriment of other compositions. All this is due to the thermal decomposition of free radicals of the load processed [21].

CONCLUSIONS

In this study, we investigate the phenomenon of thermal cracking during vacuum distillation of atmospheric residue of origin Arabian Light with an increase of the distillation temperature from 380 to 400 °C with 2 °C steps.
The main aspects observed of thermal cracking during the vacuum distillation as undesirable phenomenon have been characterized by the displacement of the cutting

points of the vacuum distillates. The depletion of total vacuum residue, the increase in performance of incondensable gas and transfer of undesirable elements as the Nickel, vanadium, asphaltenes and hydrocarbons polyaromatic cyclical from vacuum residue to the distillates with high concentrations. This is based on the use of the set of methods of analysis, which we have to allow, for well know the mechanism of thermal cracking and the problems generated by the latter in order to better optimize and improve the performance of the vacuum distillation unit.

Our study based on these analyses of the different products removed from the vacuum column in order to establish a mathematical model which relates the vacuum distillation temperature with the results of the analyses obtained for the vacuum distillates and vacuum residue. This is for a better working and performance of the vacuum distillation unit.

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