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Upgrading of heavy crude oils: Castilla

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ABSTRACT

Oil resources similar to WTI and Brent crude oils are dwindling, so heavy and extra-heavy crude oils, and bitumen must be used to meet the growing demand for fuels. The vast majority of the world's refineries are not suitable for processing these types of feed stock, so upgrading processes are required to make synthetic crude oils from those resources compatible with the equipment installed. By its viscosity Castilla crude oil is not classified as an extra-heavy crude oil, as even on surface it flows. However, it has 45.6 wt.% of vacuum bottoms and high concentrations of Conradson Carbon (CCR of 34 wt.%) and metals (nickel and vanadium content of 928 ppm) within it.

This article presents various alternatives for the upgrading of the crude Castilla, using as raw material crude oil free of lights (199 °C^{+}), reduced crude (370 °C^{+}) and vacuum bottoms. The technologies used in the studied scheme were visbreaking (VBK), delayed coking (DC), solvent deasphalting (DAF), hydrotreating and distillation. The studies were conducted at pilot plant scale and the analysis of the products was done using standard techniques such as ASTM. Among the outstanding results we have the operational scheme of the vacuum bottoms Visbreaking, but this is not a typical Visbreaking process because the coke production was 8.2 wt.%. A furnace with some characteristics of a DC furnace, and a pair of soakers that function as coking drums should be used to avoid coke deposition within the internal walls of the coils. This is an innovative technology that sits between visbreaking and delayed coking.

1. Introduction

The world needs energy, and the best source, crude oil, is scarce. It is increasingly difficult to find light crudes with low-sulfur, and low acidity. Heavy crude oils, whose reserves exceed 6 trillion barrels [1], are quite the opposite, with high concentrations of coke promoters (CCR and asphaltenes), high concentrations of sulfur, high levels of acidity and difficult to transport because they are very viscous or even solid when recovered from the producing wells. In addition, traditional refineries are not suitable for their processing, thus it is necessary to transform them into synthetic crude oils of a similar composition, either light or medium crude oils.

Today, synthetic crudes are part of the basket of crudes offered in the market, and are being processed mainly in North American refineries. Such is the case of synthetic crude oils produced from heavy and extra heavy crudes located in the Orinoco Belt (Venezuela), and tar sands from the Province of Alberta (Canada). However, there will be an increased production of heavy and extra heavy crude oils in several regions like the Gulf of Mexico and Northeastern China, as there is a necessity to replace the declining production of conventional middle and light oil over the next two decades. Nowadays, heavy and extra heavy oils are cheaper than conventional petroleum and the refining margin can be bigger if properly handled with higher profits per barrel. Besides the production of synthetic crudes from heavy crude oils and bitumen, there is the problem of their transportation by pipe line because of their high viscosity and high concentration of contaminants, problems that are avoided by their upgrading, which produces a syncrude with higher API gravity, lower viscosity and less concentration of contaminants like sulfur, nitrogen and acidity [2].

Heavy crude oils can be upgraded through various existing processes [3–5], combining different technologies: fractionation and thermal (visbreaking — VBK and delayed coking — DC) [6]. The DC is mainly applied to remove carbon and sulfur, and HDT technology is applied to stabilize the liquids and to remove sulfur and nitrogen. Solvent deasphalting process (SDP) such Kerr-McGee's ROSE (Residue Oil Supercritical Extraction) and UOP's DEMEX are still two SDA processes of high importance in the world [7,8].

The catalytic cracking process is not applied for the first step of upgrading because of the high concentration of catalyst contaminants within the feed stock: asphaltenes and resins that increase coke formation, sulfur and metals like Ni and V that are catalyst poisons. Because of that, thermal cracking is the preferred route to the upgrading of bitumen and heavy crude oil.

In addition to these well-known technologies, there is noticeable effort of researchers for reaching more efficient ways of production and upgrading bitumen and heavy crude oils using different approaches such as hydrotreating using cheap hydrogen produced

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from wind energy [9], applying solar energy for bitumen recovering from sand [10], studying the reactivity of the greater sources of heavy crude oils and bitumen like Athabaska bitumen [11], or looking for non conventional ways of bitumen processing [12].

As a result of the application of these technologies, relatively light crude oils with low yields of vacuum bottoms, and high yields of middle distillates and diesel with low concentration of sulfur and nitrogen are obtained. These features allow its use as part of the diet of crude in the refinery to improve production of medium fuels such as diesel and Jet of excellent quality.

The objective of the present study was to visualize alternatives of producing synthetic crude from Castilla crude, compatible with the existing technologies available in the refineries, at the lowest possible cost and with the best cost/benefit ratio, using well-known technologies applied for the heavy crude oil upgrading in both Orinoco belt (Venezuela) and Alberta province (Canada), the greater source of synthetic crude. Castilla crude has the following characteristics: viscosity 2297.9 cSt at 40 °C, sulfur concentration 2.39 wt.%, atmospheric distillate yield 27.6 wt.%, and concentration of asphaltenes (insolubles in n-C_7) in the crude 14.09 wt.%, and in the vacuum bottom 31.08 wt.%.

2. Experimental

For the upgrading of Castilla crude oil, operational schemes that combine the commercial technologies, using as raw material crude oil free of lights (199 °C^+), reduced crude, and vacuum bottoms were studied. These cuts were obtained by Castilla crude ASTM distillation. The distillation yields of the Castilla crude and the properties of the crude 199 °C^+ are given in Table 1. For the Castilla crude the amount of refined cuts are: atmospheric distillates 27.6 wt.%, and vacuum distillates 26.8 wt.%, so the amount of vacuum bottoms are 45.6 wt.%. As a reference the amount of vacuum bottoms in the medium crude oil is about 20 wt.% and in the light crude oil is about 5 wt.%. When there are no facilities for the upgrading of vacuum bottoms in the refinery, the alternatives are the production of asphalts for the pavement of the roads or the production of fuel oils by dilution with distillates or by visbreaking of the vacuum bottoms.

On the other hand, the amount of metals (Ni + V) in the Castilla crude 199 °C^+ is 500.9 ppm, in the medium crude oil is less than 50 ppm, in the demetallized oil is less than 35 ppm and in the gas oil pool to FCC is less than 10 ppm. Metals are catalyst poisons, so it is important to reduce their amount in the feeds to the catalyst processes.

The runs were performed at pilot plants designed and built at ECOPETROL-ICP [13–15]. The analysis were performed according to standard methods (such as ASTM), in the laboratories of ECOPETROL-ICP certified by ISO 9001.

Table 1
Distillation of the Castilla crude and properties of the cut 199 °C^+.

Distillation		Crude 199 °C+	
Atmospheric		*Properties*	
Gases		Density at 15 °C	1.0058
Naphthas	6.7	API	9.1
Jet	3.8	CCR, wt%	17.23
Diesel	8.0	Sulfur, wt%	2.427
AGO	9.1	Ca, ppm	10.76
Vacuum		Ni, ppm	95.64
LGO	5.6	V, ppm	405.26
MGO	12.6	Na, ppm	13.81
HGO	8.6	Sum: Ni + V	500.9
Vacuum bottoms	45.6	i-nC7, wt%	18.54
		i-nC5, wt%	28.82
		Viscosity-1, cP	227 at 100 °C
		Viscosity-2, cP	94 at 120 °C
		Basic N, wt%	0.112
		Total N, ppm	4446

The operating conditions used in the pilot plants were:

- For delayed coking: load 2000 g, temperature 510 °C, pressure 10 psig and time of run 2 h.
- For visbreaking: temperature 480 °C and residence time 60 s.
- For deasphalting the relationship of solvent/feed was 6/1 vol/vol, the bottom temperature 60 °C and the top temperature 100 °C.

The studied operational schemes were:

1. Upgrading of Castilla crude oil 199 °C^+
   1.1 n-C_4 solvent deasphalting of crude 199 °C^+ and delayed coking (DC) of its demetallized oil (DMO).
   1.2 n-C_4 solvent deasphalting of the crude 199 °C^+ and DC of the deasphalted bottoms (DAB).
2. Upgrading of reduced Castilla crude (long residue)
   2.1 n-C_4 solvent deasphalting of the reduced crude and DC of the Deasphalted bottoms.
   2.2 Delayed coking of reduced crude.
3. Upgrading of the vacuum bottoms from Castilla crude.
   3.1 Vacuum bottoms DC
   3.2 n-C_4 solvent deasphalting of the vacuum bottoms; DC of the DAB, and hydrotreating (HDT) of the coker distillates.
   3.3 Visbreaking (VBK) of the vacuum bottoms

The cut composition of each sample for each scheme was done by simulated distillation.

3. Results and discussion

3.1. Upgrading of Castilla crude oil 199 °C^+

3.1.1. n-C_4 solvent deasphalting of crude 199 °C^+ and DC of its DMO

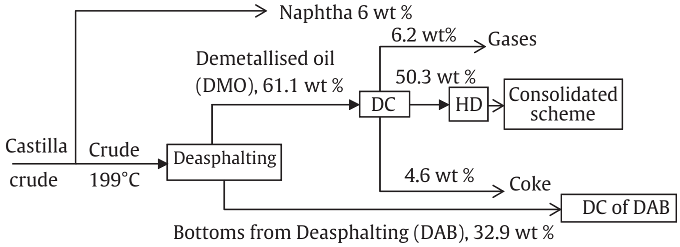
Table 2 presents the consolidated results of each scheme with respect to the original crude oil. To obtain the crude cut of 199 °C^+ the amount of naphtha withdrawal was 6 wt.%. In the process of deasphalting 61.1 wt.% of demetallized oil (DMO) and 32.9 wt.% of deasphalted bottoms (DAB) with respect to the whole crude (column 2), and 65 wt.% of DMO and 35 wt.% with respect to the crude 199 °C^+ (column 3 in bold) were produced. Within the same column the results of DMO's simulated distillation are given. In column 4 the recomposition of the whole crude is given.

The quality of the DMO obtained was similar to that of a synthetic crude, with CCR of 4.4 wt.%, however, the metals concentration, Ni = 16.6 ppm, and V = 69.5 ppm is too high (Table 3). These amounts exceed the allowable limits of metal concentrations within the DMO (35 ppm) that is processed in the traditional hydrotreating–catalytic cracking scheme. The metals are deposited on the hydrotreating catalyst surface deactivating it and reducing the turnaround of the plant from 1 year or more to just a couple of months. On the other hand, taking into account the SARA analysis, the obtained DMO is a very good feed to the DC process as its asphaltene concentration is too low (0.2 wt.%), which means high distillate yields.

The DC of the DMO produces 10.1 wt.% of gases, 82.4 wt.% of distillates and only 7.5 wt.% of coke (column 5 in bold, Table 2) as it was foreseen by the DMO's low asphaltene concentration, however, the amount of coke related to the CCR is high and is 1.7 times the amount of CCR within the feed stock. In the same column the simulated distillation of the DC distillates is given. The little coke yield is the result of coke promoter removal within the deasphalting process. Among coke promoters the insolubles in cyclohexane predominate with a concentration of 10 wt.% [16]. Within the distillates diesel and naphtha predominate.

The distillates of the DMO's delayed coking were processed in HDT (column 6), and the consolidated balance with respect to the 61.1 wt.% production of DMO is presented in column 8.

Table 2
Deasphalting of Castilla 199 °C^{+}, and DC of its DMO and its DAB.



1	2	3	4	5	6	7	8	9	10	11
		Deasphalting		Deasphalting Delayed Coking of DMO				Total DC of DMOHDT	DC of FDA	Total DC of FDA
	Crude	DMO	Total	DC	HDT-Distillates	Distillates 82.4 %	Total HDT/DMO			
Atmospheric distillation										
Gases				**10.1**		**10.1**	6.2	6.2	**7.7**	2.5
Naphthas	6		6.0	16.2	21	17.3	10.6	16.6	18.0	9.4
Jet		5	3.1	8.7	11	9.1	5.5	5.5	8.0	3.7
Diesel		12	7.3	16.9	15	12.4	7.6	7.6	15.0	9.6
AGO		13	7.9	14.2	13	10.7	6.5	6.5	14.0	10.1
Vacuum distillation										
LGO		14	8.6	12.4	13	10.7	6.5	6.5	15.0	10.8
MGO		12	7.3	8.6	12	9.9	6.0	6.0	7.0	8.4
HGO		15	9.2	4.6	12	9.9	6.0	6.0	10.0	10.7
Vacuum bottoms		29	17.7	0.9	3	2.5	1.5	1.5	13.0	19.7
DMO	61.1	**65.0**								
DAB	32.9	**35.0**	**32.9**					32.9		
DC Distillates				**82.4**					**46.4**	
Coke				**7.5**		**7.5**	4.6	4.6	**45.9**	15.1
Total	100		100.0		100.0	100.0	61.1	100.0	100.0	100.0

DC — delayed coking; DAB — bottoms from the deasphalter; DMO — demetallized oil.

This is a scheme of high production of gasoline (16.6 wt.%) and residues (32.9 wt.% of deasphalting bottoms and 4.6 wt.% of coke). The high gasoline production is due to the severe thermal process that the diesel and middle distillates undergo. The quality of the products from this scheme is presented in Table 3. The high sulfur concentration within the DC distillates is handled in the HDT process.

Table 3
Properties of the products from the crude 199 °C^{+} deasphalted with n-C_4, and of the DC distillates.

	DMO	DC of DMO	DAB	DC of DAB
Density at 15 °C	0.9546	0.9113	1.086	0.9300
API	16.6	23.7	−1.2	20.6
CCR, wt%	4.4	2.1	39.8	3.5
Sulfur	1.9	1.5	3.7	2.3
Heat of combustion	—		40.599	
Ashes, wt%	—		0.2	
Ca, ppm	17.1		21.0	
Ni, ppm	16.6		243.3	
V, ppm	69.5		981.7	
Na, ppm	49.2		67	
Sum: Ni + V	86.14		1225.0	
i-nC_7			42.9	
i-nC_5			50.8	
Viscosity-1, cP	28 at 80 °C		4,170,000 at 135 °C	
Viscosity-2, cP	14 at 100 °C		476,000 at 147 °C	
Basic N, wt%	0.07	0.065	0.254	0.118
Total N, ppm	1883	1727		3467
SARA analysis, wt%				
S	49.3			
A	40.0			
R	10.5			
A	0.2			

3.1.2. Deasphalting of the crude 199 °C^{+} and DC of the deasphalted bottoms

The deasphalted bottoms cannot be processed in the visbreaker due to their high concentration of coke promoters (39.8 wt.% of CCR). Usually the CCR concentration within the feed to the visbreaking process is lower than 20 wt.%. Because of that, the alternative process is the DC.

Within column 10 of Table 2 in bold the yields of coke, distillates and gases are given. The coke yield is 45.9 wt.% which is significantly lower than expected. According to the University of Tulsa [17], the amount of expected coke for feed stocks having 20–27 wt.% of CCR is 1.5 times the amount of CCR, and for this case is $1.5 * 39.8$ wt.% = 60 wt.%. Considering the type of feed stock, the distillate yield is very high (46.4 wt.%); the gas production is 7.7 wt.% (column 10 in bold). In the same column the simulated distillation of the DC distillates is given. The only explanation for the high distillate yield taking in account the high coke promoter's concentration in the feed stock is that the asphaltenes have high concentrations of naphthenic and paraffinic carbons within their micelles.

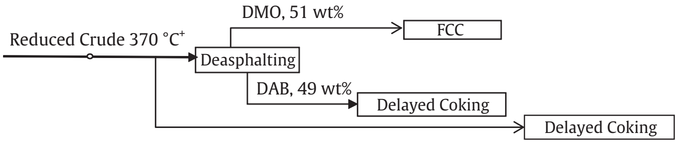
In column 11, the composition of the synthetic crude obtained from the scheme of the deasphalting of crude and DC of the bottoms from the Deasphalted is given.

In both DC schemes studied, the concentration of sulfur is reduced with respect to the value of the raw material (Table 3). The same applies to the CCR, which is reduced in the first scheme from 4.4 wt.% to 2.1 wt.%, and in the second scheme from 39.8 wt.% to 3.5 wt.%. The CCR reduction is due to the conversion of coke promoters in coke, which also leads to the reduction of sulfur because of its association with coke promoters.

3.2. Upgrading of reduced Castilla crude

These alternatives preserve the atmospheric distillates quality and seek to maximize the middle distillates' production (Table 4).

Table 4
Alternatives for the upgrading of Castilla reduced crude oil.



1	2	3	4	5	6	7	8	9	10	11	12	13
			Scheme DA–DC of DAB							Scheme DC of R. Crude		
	Crude	RC	DA/RC	DMO	DMO at 51 wt.%	DAB	DC of DAB	DC of DAB at 49 wt.%	DMO + DC of DAB	DC of RC	HDT	Total/crude
Atmospheric distillation												
Gases							13.0	6.4	4.6	7.2	7.2	5.2
Naphthas	6.7						8.0	3.9	9.5	15.7	15.2	18.0
Jet	3.8	1					3.4	1.7	5.0	7.5	8.1	9.2
Diesel	8.0			2	1.02		5.3	2.6	10.6	13.6	14.5	17.9
AGO	9.1	3		7	3.57		5.5	2.7	13.6	15.8	16.5	20.5
Vacuum distillation												
LGO	5.6	11		18	9.18	5	7.2	3.6	9.2	9.1	9.0	6.6
MGO	12.6	12		18	9.18	4	7.0	3.4	9.2	7.5	6.7	5.4
HGO	8.6	14		21	10.7	7	5.8	2.8	9.8	4.4	3.8	3.2
Vacuum Bottoms	**45.6**	59		34	17.3	84	2.8	1.4	13.6	1.1	0.8	0.8
DMO			**51**									
DAB			**49**									
DC distillates												
Coke							42.0	20.6	14.9	18.2	18.2	13.2
Total	100	100	100	100	51.0	100.0	100.0	49.0	100.2	100.0	100.0	100.0

DAB — bottoms from the deasphalter; RC — reduced crude; DA — deasphalting.

Two operational schemes were considered:

- n-C_4 solvent deasphalting of the reduced crude and DC of the deasphalted bottoms.
- DC of reduced crude.

3.2.1. *n-C_4 solvent deasphalting of the reduced crude and DC of the deasphalted bottoms (DAB)*

The objective of this scheme is to reduce technology costs required to obtain good quality synthetic crude. Taking in count the CCR concentration in the vacuum bottoms it is appropriate to consider the DC technology for their upgrading. However the DC of the reduced crude increases significantly the cost of the upgrading technology. For that reason the deasphalting process was considered as an upgrading alternative.

Deasphalting was applied to the reduced crude which represents 72.4 wt.% of the original crude (column 2 of Table 4, LGO + MGO + HGO). In column 3 the reduced crude simulated distillation is given, and within them, the vacuum bottoms correspond to 59 wt.%.

As a result of the deasphalting 51 wt.% of demetallized oil (DMO) and 49 wt.% of DAB (column 4) were produced. In column 5 the DMO's simulated distillation is given. It includes almost all vacuum gas oils and 58 wt.% of the vacuum bottoms. The extraction related to the vacuum bottoms was poor considering the asphaltene concentration within the feed (CCR = 21.4 wt.%). In column 6, the DMO production reduced to its yield (51 wt.%) is given.

Simulated distillation of DAB indicates that bottoms are mainly composed of vacuum bottoms (84 wt.%) and vacuum gas oils (column 7 of Table 4).

The DC was applied to DAB (35.5 wt.% of the original crude), and was performed at 520 °C. The yields are given in column 8. The coke production was 42 wt.%, and the gas production 13 wt.%. In column 9 the yields of DC reduced to the production of DAB (49 wt.%) are given. The coke yield is high but corresponds to the high asphaltene concentration within the feed (CCR = 38.97 wt.%, Table 5, column 4).

Table 5 shows the product quality of the studied upgrading schemes that start with reduced crude. The change trends are similar to those presented in the schemes of the 199 °C+ crude oil upgrading. The concentrations of Ni and V in the DMO of the reduced crude are lower than those presented in the DMO of 199 °C+ crude oil (Ni = 13.9 vs. 16.6 ppm, V = 45.5 vs. 69.5 ppm; see Tables 3 and 5). This is due to the atmospheric distillates present in the crude 199 °C+, which act as a heavy solvent that slightly increase the yields of DMO, but reduces their quality by increasing the concentrations of

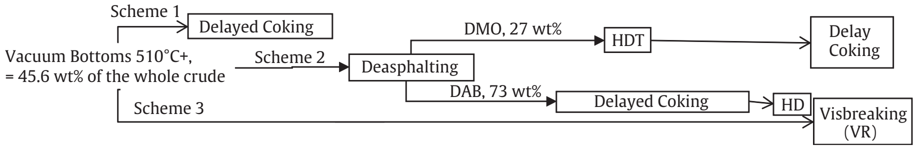
Table 5
Quality of the products obtained from the upgrading of Castilla reduced crude oil.

Properties	Reduced crude	DMO	DAB	DC of DAB	DC of R. Crude
Density at 15 °C	1.0367	0.9729	1.0483	0.932	0.9236
API	4.9	13.9	3.4		
CCR, wt.%	21.4	4.61	38.97	4.19	2.53
Sulfur, wt.%	3.1	1.952	3.65	2.2	1.98
Heat of combustion	–	–	40.549		
Ashes, wt.%	–	–	0.227		
Ca, ppm	14.7	2.23	10.04		
Ni, ppm	123.5	13.87	245.84		
V, ppm	519.8	45.52	1052.48		
Na, ppm	64.4	16.49	40.64		
Sum: Ni + V	643.3	59.39	1298.32		
i-nC_7	19.2	0.1	40.16		
i-nC_5	24.0	0.3	49.58		
Viscosity-1, cP	2070 at 100 °C	117	1,090,000 at 140 °C		
Viscosity-2, cP	1230 at 120 °C	53	370,000 at 148 °C		
Basic N, wt.%	0.1	0.1	0.2	0.133	0.1
N Total, ppm	5862	2651	9200	5395	5351
SARA analysis, wt.%					
S	19	24.2	–		
A	46.4	63.7	–		
R	15.8	12.1	–		
A	18.8	–	–		

DMO — demetallized oil, DAB — bottoms from the deasphalter, DC — delayed coking.

Table 6

Alternatives for the upgrading of the Castilla crude oil vacuum bottoms.



	1	2	3	4	5	6	7	8	9	10	11	12	13	14
		Delayed coking of vacuum bottoms			Deasphalting of vacuum bottoms				Delayed coking of DAB				VR of vacuum bottoms	
	Crude	DC	HDT of distillates	Consolidated	DMO	HDT of DMO	DMO at 27 wt.%	DAB, 482 °C	DC of DAB	HDT of distillates	DAB at 73 wt.%	Consolidated scheme	VR	Consolidated
Atmospheric distillation														
Gases		10.0	10.0	4.6					**10**	**10.0**	**7.3**	3.3	0.7	0.3
Naphthas	**6.7**	**11.9**	**11.1**	**11.7**					9.0	8.6	**6.3**	9.5	3.2	8.1
Jet	3.8	4.8	5.9	6.5					3.9	4.7	3.5	5.4	2.0	4.7
Diesel	8.0	7.3	8.3	11.8					6.0	6.6	4.8	10.2	4.1	9.9
AGO	9.1	6.5	7.2	12.3		2	0.5		5.4	5.9	4.3	11.3	6.7	12.1
Vacuum distillation														
LGO	5.6	6.9	7.4	9.0		3	0.8		5.8	6.3	4.6	8.1	1.0	6.1
MGO	12.6	6.9	6.9	15.7	6.0	8	2.2	1.0	6.1	6.1	4.5	15.6	1.4	13.2
HGO	8.6	7.4	6.7	11.7	34.0	31	8.4	8.0	7.1	6.3	4.6	14.5	11.5	13.9
Vacuum bottoms	45.6	3.1	1.5	0.7	60.0	56	15.1	91.0	3.7	2.4	1.7	7.7	51.4	23.4
DMO					**27**									
DAB								**73.0**						
Coke		35.0	35.0	16.0					**43.0**	**43.0**	**31.4**	14.3	18.0	8.2
Total	100	100	100.0	100.0	27.0	100.0	27.0	73.0	100.0	100.0	73.0	100.0	100.0	100.0

DC — delayed coking, DAB — bottoms from the deasphalter, VR — visbreaking.

metals and CCR. However the sum of metals is too high for hydrotreating in order to improve the feed to the FCC process.

In column 10 (Table 4) the consolidated results for the scheme composed of atmospheric distillates plus the products from the deasphalting of the reduced crude and DC of the DAB are given. With respect to the original crude oil, a high yield of gasoline is detected.

3.3. Delayed coking of reduced crude

Normally delayed coking has excellent feed flexibility and it can process feedstocks with large CCRs, however CCR values above 27 wt.% increase the coke yield significantly and the process becomes too expensive. Castilla crude vacuum bottoms significantly overcome that value, which suggests that for this technology the reduced crudes should be processed instead of their vacuum bottoms.

Castilla reduced crudes correspond to 72.4 wt.% of the total crude oil, which implies a significant increase in the processing capacity of the DC, but at the same time implies greater conversion, highlighting the high production of diesel and naphtha. The coke production is similar to the previous scheme and corresponds to 13.2 wt.%. In column 11, (Table 4) the yields from the DC of the reduced crude are given; in column 12 the hydrotreating of DC distillates is given, and in column 13 the synthetic crude which includes the atmospheric distillates plus the products from the DC of the reduced crude is given.

In comparison to the previous scheme, this is a scheme of high atmospheric distillates and lower yields of vacuum distillates. All distillates need HDT processing as they are unstable and can't be blended with finishing distillated products as jet or kerosene.

3.4. Upgrading of the vacuum bottoms from Castilla crude

The alternatives for the upgrading of the vacuum bottoms are:

- Delayed coking of the vacuum bottoms and HDT of distillates.
- n-C_4 deasphalting of the vacuum bottoms; DC of the DAB, and HDT of the coker distillates.
- Visbreaking (VBK) of the vacuum bottoms and HDT of the VBK distillates.

All consolidates are presented in reference to the original crude oil and correspond to the synthetic crude oils.

3.4.1. Vacuum bottoms DC (Table 6, columns 2–4)

In this scheme the upgrader capacity is reduced because only vacuum bottoms are processed (45.6 wt.% of the crude oil). The naphtha production in the synthetic crude with respect to the original oil nearly doubled, from 6.7 wt.% to 11.7 (columns 1 and 4). The sum of jet plus diesel increases from 11.8 wt.% to 18.3 wt.%. The gas oil production increases from 35.9 wt.% to 48.7 wt.%, and the coke production is 16 wt.%. The amount of CCR in the feedstock is 31.2 wt.% which according to the rule of thumb means $31.2 \times 1.5 = 46.8$ wt.% of expected coke yield with respect to the vacuum bottoms, however the real coke yield was 35 wt.%. This value is too low and suggests

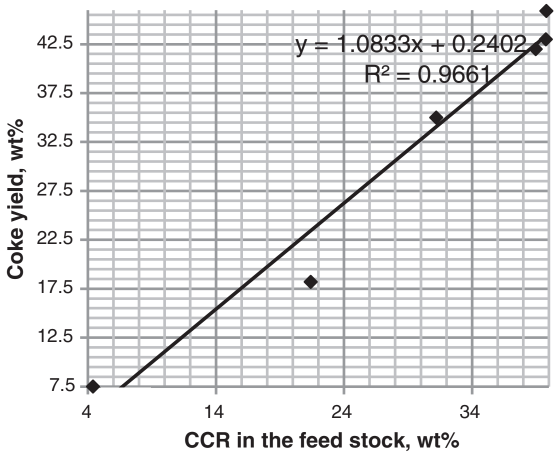


Fig. 1. Correlation between coke yield and CCR in the feed.

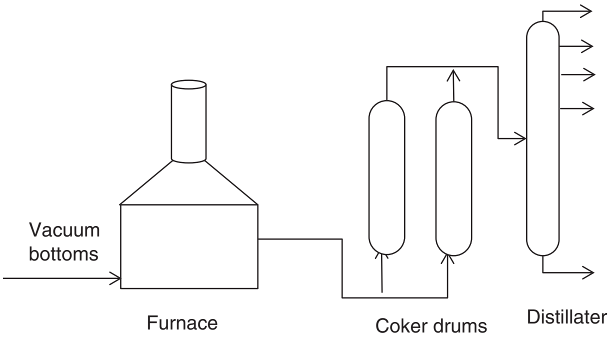


Fig. 2. VBK of the vacuum bottoms with coker drums as soakers.

that for feedstocks having CCR values higher than 25 wt.%, the multiplier for the rule of thumb should be less than 1.5.

The HDT of the DC distillates increases the production of jet, diesel, GOA, and LGO due to the conversion of some molecules of heavy gas oil and vacuum bottoms to lights.

3.4.2. n-C4 solvent deasphalting of the vacuum bottoms (Table 6, columns 5–8); DC of the DAB, and HDT of the Coker distillates (Table 6, columns 9–12)

The DMO yields (27 wt.%, in bold) and the simulated distillation of the DMO are given in column 5. The results of the DMO hydrotreating are given in column 6, and in column 7 we have the same results as column 6, but are taken to the sum of 27 wt.% (the yields of DMO).

The yields of the DAB (73 wt.%, in bold), and their simulated distillation are given in column 8. The yields of the DC of DAB are given in column 9; the distillates from the DC are hydro-treated and the yields are given in column 10. In column 11 we have the same results as column 10 but are taken to the sum of 73 wt.% (the yield of DAB). The consolidated scheme is given in column 12.

The low DMO yield means that the vacuum bottoms are composed mainly of asphaltenes. That corresponds to the concentration of insolubles in n-C_7 (28.81 wt.%) within the feedstock.

In the DC of the DAB the coke yield with respect to the vacuum bottoms is 43 wt.%, and with regard to the crude oil is 14.3 wt.%. That value is too high, however it should be considering that the concentration of CCR within the feedstock is 39.76 wt.%, and that the coke prediction according to the rule of thumb should be $39.76\times1.5=59.6$ wt.%. That result confirms that for a feedstock having a CCR concentration higher than 25 wt.% the multiplier factor for coke forecast should be 1.1 times the concentration of the CCR within the feedstock. The HDT of the DMO produces a slight conversion of heavy gas oil (HGO) and vacuum bottoms to middle vacuum gas oil (MGO), light vacuum gas oil (LGO) and AGO as shown in the comparison between the columns 3 and 4 (Table 6). The HDT of DC distillates register a similar pattern to that of the HDT of the DMO.

In general, it was observed that the yield of coke in the DC process is about 1.1 times the amount of CCR in the feed stock as can be seen from Fig. 1. This result is very important for take decisions about the scheme that should be chosen for the upgrading of heavy crude oils because the rule of thumb followed for the refineries is 1.5 times the amount of CCR in the feed stocks, and this value is very high.

The results of the comparison between the schemes of VB DC (Table 6 column 4) and n-C_4 solvent deasphalting of the vacuum bottoms and DC of the DAB, and HDT of the coker distillates(Table 6, columns 12) show that both schemes arrive at similar yields of distillates and coke.

3.4.3. Visbreaking (VBK) of the vacuum bottoms (Table 6, columns 13–14)

In column 13 the yields of the vacuum bottoms visbreaking are given, and in column 14 we have the synthetic crude of this scheme.

Table 8
Technology costs.

	Value of the technology US$/Bl	Taken value US$/Bl
Atmospheric distillation		1000
Atmospheric and vacuum distillation	750–2200	2000
Deasphalting	1850–8000	4000
Delayed coking	5800–12,000	8000
Hydrotreating	3000–3500	3000
Visbreaking	1800–3500	3000
Crude for the process, bl/day		50,000

Table 7
Quality of the products from the upgrading of the vacuum bottoms obtained from the Castilla crude oil.

Properties	Vacuum bottoms (VB)	DC of Vacuum bottoms	DMO	DAB	DC of DAB	VB of vacuum bottoms visbreaking
Density at 15 °C	1.036	0.9182	0.9854	1.0537	0.929	1.081
API	5		12	2.7		-0.6
CCR, wt.%	31.2	4.21	6.88	39.76	5.41	38.5
Sulfur, wt.%	3.48	2.18	2.473	3.8	2.44	3.22
Heat of combustion	–		–	40.455		40.6
Ashes, wt%	–		–	0.226		
Ca, ppm	4.77		2.1	5.18		14.75
Ni, ppm	185		19.81	232.91		206
V, ppm	735		72.81	1014.83		802
Na, ppm	25		7.68	39.58		44
Sum: Ni + V	920		92.62	1247.74		1008
i-nC_7, wt.%	28.81		–	40.98		20.7
i-nC_5, wt.%	35.6		–	47.86		36.8
Viscosity-1, cP	1,217,082 at 40 °C		959 at 80 °C	4,400,000 at 140 °C		578,000 at 120 °C
Viscosity-2, cP	233,653 at 50 °C		270 at 100 °C	1,010,000 at 148 °C		279,000 at 135 °C
Basic N, wt.%	0.203	0.129	0.098	0.189	0.143	0.253
Total N, ppm	7625	6973	3410	–	7455	10,105
N.N, mg KOH/g						0.6
SARA analysis, wt.%						
S	9.2		24.5			11.6
A	42.3		61.1			44.9
R	19.6		14.4			22.8
A	28.9		–			20.7

VB — vacuum bottoms, DC — delayed coking, DAB — bottoms from deasphalting.

Table 9
Investment cost of the proposed schemes.

	Economic impact of the studied upgrading alternatives of the Castilla crude	MMUS$
1	Visbreaking (VR) of the vacuum bottoms and HDT of the distillates from VR	224
2	Deasphalting of crude 199 °C + and DC of its DMO	250
3	Deasphalting of the crude 199 °C + and DC of the bottoms obtained in the deasphalting.	250
4	DC of the vacuum bottoms and HDT of DC distillates	351
5	n-C4 deasphalting of the vacuum bottoms; DC of the DAB, and HDT of the distillates from DC	374
6	n-C4 deasphalting of the reduced crude and DC of the deasphalted bottoms	390
7	Delayed coking of reduced crude	448

With regard to the vacuum bottoms, a high yield of coke (18 wt.%) is detected, which is unusual in the VBK technology (the usual values are less than 1 wt.% at pilot plant scale). However, with respect to the crude oil, the coke production is only 8.2 wt.%. In contrast there was a significant reduction in the vacuum bottoms within the synthetic crude oil which reduced from 45.6 wt.% to 23.4 wt.%.

The VBK process of a feed stock that produces high levels of coke is inconvenient because it means that the plant should be shutting down every day for cleaning. An alternative to improve this effect is to install two soakers in parallel, which operate in a similar way as the coker drums, but with the residence time reduced to 7 min (Fig. 2). This way there will be an upgrading scheme of low conversion, low investment and low coke yield. An additional advantage of this process is the reduction of the crude oil viscosity for its transport by pipeline. The distillates from this synthetic crude should be hydrotreated because they are unstable and have high sulfur concentrations.

Table 7 shows the quality of products from the upgrading of the Castilla crude oil vacuum bottoms. The CCR is reduced from 31.2 wt.% in the vacuum bottoms to 4.2 wt.% in the DC distillates from the vacuum bottoms and to 5.4 wt.% in the distillates from DC of DAB. The DMO from the vacuum bottoms has a CCR of 6.9 wt.%. The scheme of vacuum bottom deasphalting and DC of the DAB shows yields and qualities similar to those given by the vacuum bottoms DC scheme.

3.4.4. Cost of technologies for evaluated schemes

The calculations were performed with the values presented in Table 8 [18] and on the basis of 30,000–50,000 barrels/day.

In Table 9 the values of the different technological alternatives for the processing 50 KBPD of crude Castilla are given. The lower cost alternative is the visbreaking of the vacuum bottoms and hydrotreating of the distillates obtained from the VBK, followed by the alternatives of deasphalting of the crude and DC of the DMO or the DAB. Between the last two alternatives, the better conversion is obtained in the alternative of deasphalting of the crude 199 °C$^+$ and DC of the DAB.

4. Conclusions

Of all alternatives studied, the visbreaking of the vacuum bottoms is the most economical and innovative alternative, taking into account that it combines a furnace that operates at the visbreaking conditions, but includes design elements of DC furnace to control the accumulation of coke in the coils. Furthermore in this arrangement there are coke drums instead of soakers for accumulation and withdrawing of produced coke during the process. The residence time in the coking drums is about 5–7 min. Additionally, this scheme maintains the yields of the atmospheric distillates and stabilizes distillates (HDT) from the visbreaking process.

Another aspect to highlight for coke yield prediction according to the rule of thumb is that as the CCR concentration in the feed stocks is increasing, the multiplier number of the CCR is reduced: for feed stocks having a concentration of CCR lower than 5 wt.%, the yield of coke is 1.7 times the concentration of CCR in the feed stocks. For feed stocks having a concentration of CCR higher than 25 wt.%, the yield of coke is about 1.1 times the amount of CCR in the feed stocks. Applying the formula:

$$\text{Coke yield, wt.\%} = 1.0833 \times \text{CCR (wt.\%)} + 0.2402$$

the coke yield is quite well predicted knowing the CCR concentration in the feedstock.

Nomenclature

DAB	deasphalted bottoms
DMO	demetallized oil
DC	delayed coking
HDT	hydrotreating process.
LGO	light vacuum gas oil
MGO	medium vacuum gas oil
HGO	heavy vacuum gas oil
AGO	atmospheric gas oil
VBK	visbreaking
R. Crude	reduced crude

References

[1] J. Plotkin, Exploiting unconventional heavy oils, in: PTQ — Q1, 2007, pp. 65–67.
[2] R. Martínez-Palou, et al., Transportation of heavy and extra-heavy crude oil by pipeline: a review, Journal of Petroleum Science and Engineering 75 (2001) 274–282.
[3] M. Rana, et al., A review of recent advances on process technologies for upgrading of heavy oils and residua, Fuel 86 (2007) 1216–1231.
[4] Le Page, J., Chatila, S. and Davidson, M. Residue and heavy oil processing. Editions. Technip, Paris, 1992
[5] M. Gray, Upgrading Petroleum Residues and Heavy Oils, Marcel-Dekker, 1994.
[6] J. Speight, in: Chapter 5: Thermal Cracking The Refinery of the Future, and Hydrotreating (HDT), 2011, pp. 147–180.
[7] J. Gearhart, L. Garwin, Resid-extraction process offers flexibility, Oil and Gas Journal 74 (1976) 63–66.
[8] R. Newcomer, R. Soltau, Heavy oil extraction ups FCC feed at first three-stage grass roots ROSE unit, in Kansas, Oil and Gas Journal 80 (1982) 108–110.
[9] B. Olateju, A. Kumar, Hydrogen production from wind energy in Western Canada for upgrading bitumen from oil sands, Energy 36 (11) (2011) 6326–6339.
[10] D. Kraemer, et al., Solar assisted method for recovery of bitumen from oil sand, Applied Energy 86 (9) (2009) 1437–1441.
[11] P. Danial-Fortain, et al., Reactivity study of Athabasca vacuum residue in hydroconversion conditions, Catalysis Today 150 (2010) 255–263.
[12] Wahyudiono, et al., Non-catalytic liquefaction of bitumen with hydrothermal/solvothermal process, Journal of Supercritical Fluids 60 (2011) 127–136.
[13] J. Carrillo, F. Pantoja, G. Vela, Visbreaking pilot plant, in: Gaceta 444 del 7 de Mayo, 1997, p. 200.
[14] J. Carrillo, F. Pantoja, G. Vela, Liquid–liquid in continuous extraction pilot plant, in: Gaceta 448 del 9 de Julio, 1997, p. 216.
[15] J. Carrillo, H. Picón, L. Garzón, L. Corredor, Delayed coking: Castilla and Jazmín crude oils, ACS National Meeting, Fuel Chemistry 52 (2007) 2.
[16] J. Carrillo, L. Corredor, M. Valero, Characterization and studies of kinetic and severity in the visbreaking of heavy crude oils: Castilla, Rubiales, and Nare-Jazmín, ACS National Meeting, Fuel Chemistry 49 (2004) 2.
[17] M. Volk, et al., Fundamentals of delayed coking, Joint Industry Project, University of Tulsa. Departamento f Chemical Engineering, 2002.
[18] Refining Processes Handbook 2011. Hydrocarbon processing