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Additional Information



Alternative to visbreaking or delayed coking of heavy crude oil through a short contact time, solid transported bed cracking process

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An extra-heavy crude oil was treated at short contact time in the 510–580°C temperature range in a FCC-like process, first thermally and then in the presence of a solid with low catalytic activity. The treatment improved greatly the properties of the crude oil, reducing density and viscosity to values that makes the oil transportable without dilution in pipeline. Besides, the upgraded was substantially free of contaminants such as metals and heptanes insolubles. The use of the solid allowed upgrading all properties with a minimum coke penalty. The residual fraction of the upgraded oil had to be eliminated to obtain a syncrude stable in asphaltene proof, which could be obtained by recycling to extinction in the cracking reactor.

Broader context.

In spite of increased efficiency of ICE engines as well as the emergence of electric vehicles, demand for liquid fuel will remain strong due to a steady increase in vehicle fleet size. Biomass-based fuels may meet a small part of the demand, notwithstanding relying heavily on petroleum based fuels. While conventional crude oil may be in tight supply, a number of extra-heavy oils reserves are accessible, yet remain challenging to market due to the properties of the oil. Upgrading the oil before entering the refinery or even for enabling transportation is often necessary. While thermal processes suited for this class of feed (or resid processing) such as visbreaking or delayed coking can be used for this purpose, refining technology may be extended into improved processes including some active material for generating more syncrude with lower contaminants such as metals and asphaltenes.

1. Introduction

As the reserves of cheap, conventional crude are declining, new resources are coming on stream to fulfil the increasing demand on transportation fuels. A number of synthetic crudes can be obtained from unconventional sources, such as extra-heavy crude oils or lignocellulosic biomass, and be further processed in existing or upgraded refinery processes, thus taking advantage of the huge oil processing infrastructure already available. Nevertheless they raise a number of problems due to their composition that requires solutions.

Extra heavy crude oil, defined as having an API lower than 10 (denser than water) contains much more contaminants (asphaltenes, metals) than traditional crude oil, and resembles low quality resid. Although tractable, resid upgrading is difficult,

requiring harsh processing conditions for obtaining transportation fuels. Another problem lies on the well-to-refinery crude transportation, since high viscosity and high density makes these oils not compatible with pipeline specifications, requiring for example the use of diluents.^{1,2} Yet the diluent (e.g. naphtha) has to be shipped to an often remotely located oil production site, which creates logistical issues. Once delivered to the refinery, the upgrading of such crude is also challenging due to its metal (Ni, V, Fe) and Carbon Conradson Residue (CCR) content, which are far beyond current levels found in crude oil. Significant upgrading is then required upfront the refinery. Thus, a simple and robust upgrading process is highly desirable to be eventually deployed at or close to the oil generation site.

A number of processes for this purpose were reviewed by Castañeda et al.³ Then, hydrotreating requires producing hydrogen and cannot treat the worst crudes due to excessive catalyst contamination. Coking or visbreaking processes may be used, generating a higher oil quality and a variable amount of coke.^{4,5} Thermal cracking using sand in circulating beds, inspired from FCC technology and adapted to biomass conversion, were developed, such as the Heavy To Light (HTL) process.^{6,7} Contacting heavy oil with hot sand under short residence time is also carried out in the Viscositor process.⁸ It has also been proposed to couple a thermal cracking fluid bed

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to a catalytic cracking reactor for optimal processing of heavy crude fractions in the refinery.⁹ All these processes use sand as heat carrier in a purely thermal process. Other promising processes that still need substantial development include aquathermolysis and upgrading with methane. Aquathermolysis may be performed in the presence of catalyst (mineral, water- or oil-soluble, dispersed), and was also proposed to be performed down hole, taking advantage of the pressure inside the well.¹⁰ Upgrading with methane was performed on Ag-Zn/HZSM5 at 380°C, achieving significant reduction in asphaltene content with very low coke yields.¹¹

We have thus explored the use of several materials in a transported bed where the heavy oil upgrading is performed at short contact time, supplementing thermal cracking with some catalytic function in order to obtain an improved crude, less dense and more fluid but also substantially free of contaminant (metals and CCR).

2. Material and methods

2.1. Heavy oil and cracked liquid products characterization

An extra-heavy crude oil from the Chichimene oil field, stripped of gasoline fraction, whose properties are summarized in Table 1, was used in the study. It contained 15 wt% of diesel-range products, and 45% vacuum bottoms. Density was measured with an Anton Paar DMA4500 densimeter at 1.02 g·cm⁻³ at 15°C, slightly above water density. It began to flow at 80°C, so that viscosity was measured at 100°C. Conradson Carbon was measured at 17 wt% (Micro Carbon Residue Tester, MCRT-160, Alcor), similar to the value determined through n-heptane insolubles. Metal content was measured by X-ray fluorescence (MiniPal4, PANalytical) and giving 250 ppm V and 80 ppm Ni. This value is considerably higher than what can be found in traditional crude oils.¹² A modified, manual version of ASTM 7157 was used to assess the stability of crude oil and cracked liquids. A sample of the oil to be evaluated (2g) is mixed with 10 ml of a solvent mixture of o-xylene and iso-octane (70/30 wt%) in a glass tube. The mixture is then homogenized, and a drop is deposited on a Whatman paper. The presence of flocculated asphaltenes is determined by visual inspection, as these form a black mark in the middle of the stain formed after the dispersion of the drop on the paper.

If no black mark appears using that solvent composition, the asphaltenes contained in the oil (if any) did not flocculate and the oil is considered stable enough to be transported by pipeline.

Table 1. Physicochemical properties of the extra heavy oil

Property	method	value
density (15°C, g·cm ⁻³)	ASTM5002	1.017
°API		7.6
Viscosity (cst @ 100°C)	ASTM445	498
Metals, ppm		
Vanadium	FRX	250 V
Nickel		82 Ni
CCR	ASTM 4530	17.6%
n-heptane insolubles	ASTM 3279	15.4%
Sulfur (wt%)	FRX	3.2
Distillation cuts (wt%)	ASTM 1160	
diesel (216-359°C)		15
VGO (359-537°C)		40
Resid (>537°C)		45

2.2. Materials

Solid heat carrier. An inert solid must be used as a heat carrier in the setup to provide heat for vaporization and thermal cracking. While the wall may transfer some heat to the gas media, it is preferable to have a solid in the unit acting as thermal mass and providing efficient heat transfer for feed vaporization and compensate for heat of reaction. Quartz sand is often used for testing thermal cracking, but due to its surface roughness and particle size (0.2 mm) it tended to form plugs in the narrow solid feeding lines of our transported bed laboratory unit, which was designed to handle Fluid Catalytic cracking catalysts. Thus, an inert solid was prepared from an equilibrium catalyst, which was impregnated with a solution of sodium carbonate, then steamed at high temperature (850°C during 10 h under 100% vapor) to ensure vitrification of the catalyst. As a result of the treatment, the BET surface area was reduced below 1 m²·g⁻¹ and micropore volume was inexistent. Bulk density increased slightly to 1100 kg·m⁻³ due to the shrinkage of porous network. No acidity could be detected through pyridine desorption experiments. The solid retained the typical shape of FCC equilibrium catalyst from which it was prepared (0.06 to 0.1 mm microspheres), having excellent fluidization properties.

Activity and selectivity of this material was tested in the cracking of a standard Vacuum Gas Oil and compared with that of Silicon Carbide (Carborundum®). The prepared inert solid showed identical yields of gas, distillates and coke than the reference material for thermal cracking, and thus was considered totally inert.

Silica-alumina. A commercial silica-alumina was used with a Si/Al ratio of 2, measured by ICP. It was shaped in microspheres of 0.06-0.10 mm compatible with standard FCC equipment. This additive was steamed for 4 hours at 820°C with 100% steam before use. Its surface area was then reduced to 85 m²/g. It was used without further treatments.

Kaolin. A commercial sample of acid treated kaolin was used. It was shaped in microspheres of 0.05-0.20 mm compatible with standard FCC. The fraction 0.10-0.20 mm was removed for proper flowing in the experimental unit. This kaolin had a

surface area of 10 m²/g, a pore volume of 0.15 cm³/g and was used without further treatment.

2.3. Distillation and Cracking unit

Fractionation of reaction products was carried out following ASTM D-1160 standard specifications.

The MicroDowner unit is a laboratory scale transported bed unit which was designed primarily for catalytic cracking testing. Main features of the unit comprise: a) a catalyst preheater where the catalyst is stored before the test and preheated to typical regenerator temperatures; b) a once-through tubular reactor, where the feed and the preheated catalyst are contacted continuously at a short residence time (0.3 – 2.0 s); and c) a disengager in which catalyst is separated from hydrocarbons before regeneration. Schematics of the unit can be found elsewhere.¹³ Preheated catalyst and hydrocarbon are fed at a constant rate during the run to simulate a steady state during a relatively short period (1 to 4 minutes) in order to spare catalyst and feed. Nitrogen is added with the catalyst to facilitate its transport to the unit and with the feed to assist dispersion and evaporation, in a total amount equivalent to 15 wt% of the feed. The catalyst, which is continuously separated from the reaction products on a metallic porous plate during the reaction step, is stripped during an additional 60 seconds after the reaction step ended. Liquids are condensed into glass traps maintained at sub-zero temperature and gases are recovered in a gas bag. Nitrogen fed to the reactor is used as internal standard to determine final gas volume. After stripping step, coke yield on the solid heat carrier is measured by combustion with air and measuring the amount of CO₂ formed. Gas composition was determined using a GC fitted with 3 detection lines: one for H₂ separated on a 5A mol sieve and detected on a TCD, one for N₂ separated on a 13X mol sieve and detected on TCD and a third one equipped with Al-plot column and FID detector for hydrocarbons detection. Some light gasoline components were not captured in the condensing traps and were dragged to the gas collector. This fraction was properly quantified on GC and its PIONA composition determined using a 100m petrocol column and DHA[®] software from VARIAN. It represented 2-8 wt% of the oil fed and contained over 50 wt% of C₅-C₇ olefins.

Liquids were weighted and composition determined following ASTM-2887 SIMDIS method. The different fractions and their respective cut points were: gasoline (ibp-216°C), LCO (316-359°C), HCO (359-537°C) and resid (537°C-fbp). The unit was designed to treat 20-30 grams of heavy oil per test, in order to generate enough liquid products (15-20 g) to perform the different characterizations (density, viscosity, CCR, heptane insolubles and metals).

Solid to oil ratio was calculated after the test as the amount of solid recovered from the separator divided by the sum of the products recovered (gas, liquids and coke). Conversion was defined as the sum of gas, coke and gasoline yields. Gas residence time in the unit was estimated taking into account reactor size, temperature and pressure, oil feed rate (7 g/-min

¹), an oil mean molar mass of 500 g·mol⁻¹, nitrogen feed rate, and the product composition at the outlet of the unit.

3. Results and discussion

3.1. Experimental range

The reaction temperature range was limited to 510-580°C. Some testing was performed below 510°C but revealed that the vaporization of the feed, even with the amounts of nitrogen employed in this study, was not optimal, leading to the formation of important deposits of coke in the region of the injector. The upper temperature was limited below 600°C to avoid an excessive production of gases, as the main objective of the process is to produce a maximum amount of liquids.

The total amount of nitrogen injected with the feed and heat carrier represented 15 wt% of the feed, and is equivalent to injecting 23 wt% of water in a commercial unit. This value is significantly higher than in commercial FCC operation but will ensure better feed vaporization and lower coke yield.

Solid to oil ratio (STO) was varied in the 8-20 range, which implied solid feeding temperature in the range of 600-690°C, compatible with the regenerator temperature.

3.2. Thermal cracking

First, an inert solid was used as heat carrier. Results of the thermal cracking of Chichimene crude oil are summarized in Table 2.

Coke yield was found independent of operating conditions, with a yield fairly constant around 16 wt%. It is worth to note that this is very close to the CCR or n-heptane insoluble value, indicating these components deposit directly on the solid and crack to a very little extent.

Gas yield increased with temperature and residence time, but was not affected by solid to oil ratio as it has to be expected from a thermal reaction. Dry gas yield increased faster than LPG yield. Thermal shock effect may conduce to higher dry gas yield at lower solid to oil ratio (STO, all other conditions unchanged) as the preheating temperature of the solid is higher with higher STO, but this was not observed in our laboratory set-up, where fast and complete mixture can be achieved. Residence time effect was larger at the higher temperature, with a doubling of the gas yield when going from 0.3 to 2.0 seconds, reaching 10 wt% at 580°C.

The yield of liquids decreased from 82 to 73 wt% as the reaction temperature and residence time increased. Residual and HCO fractions were converted deeper under more severe operating conditions, increasing gasoline yield while middle distillate yield remained flat. Compared to the initial crude oil, the amount of residual fraction (boiling above 537°C) in the liquids was reduced within 68 to 78 wt%. The cracked liquids were analyzed with the same techniques than the crude oil, and the measured properties are summarized in Table 2.

Table 2. Yields and cracked liquid properties for the thermal cracking of extra-heavy crude oil in the 510-580°C temperature range.

ID	1	2	3	4	5	6	7	8	9
Temperature (°C)	510	510	510	510	545	580	580	580	580
Gas Residence time (s)	0,3	0,3	2,2	2,2	1,25	0,3	0,3	2,2	2,2
Solid to Oil Ratio (STO)	8	12	8	12	12	12	20	12	20
Conversion (wt%)	24,6	25,6	27,1	29,0	30,6	31,2	30,6	37,4	40,7
Gases(wt%)	2,4	2,6	3,4	3,5	5,1	5,8	5,2	9,0	10,3
- Dry Gas (H ₂ + C ₁ -C ₂)	1,0	1,1	1,4	1,5	2,3	2,7	2,5	4,3	5,1
- LPG(C ₃ -C ₄)	1,4	1,5	2,0	2,0	2,8	3,1	2,7	4,7	5,2
Liquids (wt%)	81,9	81,1	80,2	79,0	78,5	78,4	78,7	74,9	73,2
-Gasoline (C ₅ -216°C)	6,5	6,6	7,3	8,1	9,1	9,7	9,3	12,3	13,8
- LCO(216-359°C)	21,9	21,6	21,9	22,1	22,6	22,3	22,4	22,5	22,3
- HCO (359-537°C)	41,6	41,1	40,8	39,3	38,1	36,0	36,9	31,3	29,8
- Resid (>537°C)	11,9	11,8	10,1	9,6	8,7	10,4	10,1	8,7	7,3
Coke (wt%)	15,7	16,3	16,4	16,5	16,4	15,7	16,1	16,2	16,6
Properties of cracked liquid									
density (15°C)	0,9470	0,9466	0,9436	0,9410	0,9423	0,9479	0,9498	0,9467	0,9401
°API	17,8	17,8	18,3	18,7	18,5	17,6	17,3	17,8	18,9
Viscosity (cst, 40°C)	53	50	45	37	32	37	40	23	15
Metals (ppm)									
V	24	21	22	18	20	32	29	33	20
Ni	4	4	5	4	5	6	7	7	5
CCR (wt%)	2,9	3,0	3,1	3,1	3,5	4,8	5,0	6,2	5,4
n-C ₇ insolubles (wt%)	0,2	0,2	0,3	0,2	0,3	0,3	0,3	0,5	0,4

The properties determined from the liquids recovered from the traps were corrected to take into account the light gasoline that was not condensed in the trap (see section 2.3.), which weight amount and density was determined by GC. This does not apply to viscosity measurements.

The liquids produced through thermal cracking presented a density much lower than the original crude oil, and in the range of minimum specifications for pipeline transportation. The density only decreases marginally with the increase of processing temperature and gasoline fraction in the liquids, which may be due to an increase in aromatics at the expense of saturates in the total oil due to cracking reactions. The viscosity of the oil is also considerably lower. It decreases with processing temperature, and it is well within the limits for pipeline transportation, even without taking into account the fraction of light gasoline not condensed in the traps.

Metal content was also largely reduced, with a metal removal efficiency of 90-95%. Heptane insolubles were reduced to practically zero, indicating that nearly all asphaltenes were removed from the oil. Yet a significant amount of CCR was detected due to the presence of a remaining high boiling point resid fraction. **The ratio between CCR content of the liquids and the resid content determined by SIMDIS may present anomalously high values in some samples. This is caused by ASTM2887 SIMDIS limited accuracy in the determination of resid fraction, and tendency to underestimate this fraction.**

All the cracked liquids were found unstable in spite of a largely reduced amount of resid fraction, heptane insolubles or CCR in the liquid products, while the initial crude oil was found stable.

As a conclusion, this process is able to yield 73-82 wt% of a largely upgraded oil, with properties suitable for pipeline transportation (but for stability) and further processing in refinery.

3.3. A low cracking activity material for crude oil upgrading

The inert catalyst was replaced with a low surface area kaolin that is often used as a filler in FCC catalysts. It is often considered as an inert in Fluid Catalytic Cracking as it comes together with highly active zeolites (Y, ZSM5) and silica alumina. Yet it exhibits some acidity that may prove useful in the present process, where very active catalysts cannot be employed as they would lead to excessive yields of coke and gas. Indeed, the catalytic cracking mechanism through carbenium generation and chain cracking tends to yield shorter products in the gasoline and LPG range, at the cost of distillates.¹⁴ Hydrogen transfer mechanism can yield extra amounts of coke and provoke saturation of part of the olefins, and in particular diolefins which content is then very low in catalytic cracking products. By the contrary, the radical mechanism of thermal cracking tends to yield larger amount of dry gas and middle distillates.¹⁵

The crude oil was initially processed with kaolinite under the same operating conditions than inert solid. Indeed, some clear differences with thermal testing were found when using kaolinite (Table S1). Coke yield at the higher processing temperature (545°C or higher in Table S1) is stable at 17-18 wt%, similar to that obtained in thermal cracking.

Table 3. Yields and cracked liquid properties for the cracking of extra-heavy crude oil in the presence of kaolin in the 530-580°C temperature range.

ID	10	11	12	13	14	15	16	17	18
Temperature (°C)	530	530	530	530	555	580	580	580	580
Gas Residence time (s)	0,3	0,3	2,2	2,2	1,25	0,3	0,3	2,2	2,2
Solid to Oil Ratio (STO)	8	12	8	12	12	12	20	12	20
Conversion (wt%)	30,9	35,8	34,6	36,0	38,2	39,3	42,6	42,5	34,2
Gases (wt%)	3,2	4,6	4,0	4,9	6,7	8,4	7,6	10,1	9,9
- Dry Gas (H ₂ + C ₁ -C ₂)	1,5	2,2	1,9	2,3	3,4	4,2	3,9	5,1	5,1
- LPG(C ₃ -C ₄)	1,7	2,4	2,1	2,6	3,3	4,2	3,7	5,0	4,8
Liquids (wt%)	77,4	74,2	74,2	72,5	74,7	74,2	72,5	73,4	73,1
- Gasoline (C ₅ -216°C)	8,3	10,0	10,2	11,3	13,0	13,5	13,5	16,0	15,6
- LCO (216-359°C)	23,9	24,7	24,8	26,5	26,3	25,4	26,1	24,5	25,1
- HCO (359-537°C)	39,0	35,4	36,4	34,4	32,0	31,7	30,0	28,4	28,3
- Resid (>537°C)	6,2	4,2	4,2	3,0	3,4	3,6	2,9	4,5	4,1
Coke (wt%)	19,5	21,2	20,3	19,8	18,5	17,4	19,9	16,5	17,0
Properties of cracked liquids									
density (15°C)	0,9385	0,9303	0,9360	0,9297	0,9347	0,9302	0,9281	0,9365	0,9360
°API	19,1	20,5	19,5	20,6	19,8	20,5	20,8	19,5	19,5
Viscosity (cst, 40°C)*	25	15	24,37	19	13	12	10	12	11
Metals (ppm)									
V	9	10	10	9	11	11	10	11	10
Ni	1	1	<1	<1	<1	<1	<1	2	<1
CCR (wt%)	2,1	1,9	2,3	2,1	3,2	3,1	2,8	5,0	4,7
n-C ₇ insolubles (wt%)	0,1	0,1	0,2	0,1	0,3	0,2	0,1	0,2	0,2

At 510°C however, it increases substantially (4-5 points) probably due to desorption difficulties from the catalyst surface. Thus, the minimum cracking temperature was raised to 530°C for working with kaolinite (Table 3), where the coke yield was found to increase only 1-2 points over the stabilized value obtained at higher temperature. As for thermal cracking, Solid to Oil ratio seemed not to have an influence on coke yield. Gas yields obtained with kaolinite catalyst are slightly higher than thermal cracking yields, with a similar proportion of dry gas and LPG. As a consequence, the yield of liquids lowered slightly at 73-77 wt%, with a reduced content of resid and an increased yield of gasoline. Note that the amount of liquid product excluding the resid fraction (bp<537°C) is higher with the kaolinite (67-71 wt%) than in thermal cracking (66-70 wt%), in spite of a slightly higher coke and gas yields. As a consequence, the density of the liquid reported in Table 3 decreased compared to those reported from thermal cracking. This is clearly exemplified in Figure 1, in where it is shown that the liquid obtained from cracking with kaolinite has an API roughly 1.5 points higher than with thermal, at the same liquid yield. Other properties of the liquids also improve significantly compared to thermal cracking. Viscosity was found approximately 30 % lower, while metal content was lowered 50-80 %. Compared to the feed, metal content is reduced of more than 97 % for all the samples. A concern raised as the solid is recycled from test to test and metals accumulate on it. It is well known that metals loading of a few thousand ppm on fluid catalytic cracking equilibrium catalyst does influence drastically conversion and selectivity, yielding more coke and more dry gas.¹⁶ We have checked with kaolin that the yields from a same reaction (530°C, solid to oil of 8 and residence time of 0.3 s) did

not vary significantly after at least 40 runs (Figure S1). That corresponds to an amount of approximately 600 ppm V and 200 ppm Ni deposited on the solid (500g solid inventory, 30g of crude oil processed per test). We discarded the solid after a maximum of 50 runs to ensure metal deposition did not affect the yields reported here. It is worth to note that the absence of yield response to these metal quantities indicate that the metal effect on kaolin is greatly reduced on kaolin compared to the effects observed on fluid catalytic cracking (FCC) catalyst under similar metal loading. This is probably due to the low surface area of kaolin, while metals tends to be much more dispersed (and thus more active) on a FCC catalyst with large surface area.

Heptane insolubles remained near zero, while CCR lowered slightly compared to thermal cracking. Again, CCR increases with processing temperature. In spite of a reduced amount of residual fraction and increased gasoline in the liquids, that acts as a diluent, none of the cracked liquids obtained by processing with kaolinite was found stable when mixing with xylene-isooctane test solvent. The very low values of n-heptane insoluble indicate that asphaltenes were effectively removed from the cracked liquids. Yet the difference with CCR value indicates that resins or pre-asphaltene remained in the liquids, causing the observed solvent instability. We ensured that the solvent instability came from resid fraction (where the resins concentrate) by distilling the cracked liquids, obtaining a solvent-stable liquid (Table S3).

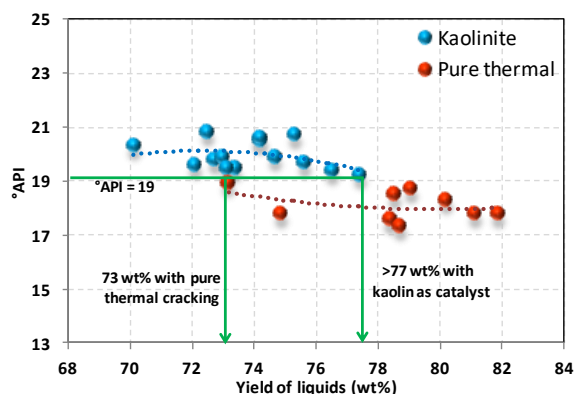


Figure 1. API degree as a function of total yield of liquids for thermal cracking and in the presence of kaolin.

As a conclusion, treating the heavy crude oil with kaolinite allows obtaining a highly upgraded liquid product, with density and viscosity values that makes them suitable for pipeline transportation. CCR, resid and metal content are similar to those found in an Arabian light crude oil.¹² The presence of a larger fraction of light gasoline in light crude oil explains the density and viscosity differences with the cracked liquids. One issue that remained is the instability of upgraded liquids, and this will be discussed below.

3.4. Optimal strategy for producing a stable upgraded oil

3.4.1. Introduction. A distillation of the cracked liquids recovered from the liquid traps showed that once stripped from the vacuum residue, the upgraded liquids were stable. While the residual fraction could be simply eliminated after distillation, this represents a significant loss of liquid yield. To avoid that loss, residual fraction could be treated in a separate coking or visbreaking process with reduced capacity, but this increases upgrading complexity. Thus, several catalyst and process options were tested to reduce or eliminate the resid fraction from the cracked liquids within the process, and thus to obtain stable liquids without significant loss of liquids. The different options studied are summarized in Figure 2.

First, a silica-alumina additive, commonly used in Fluid Catalytic Cracking, can be added to the kaolinite inventory, to in-situ reduce the resid fraction. As a second option, the resid can be flashed at the exit of the first reactor, then cracked in a second separate reactor. The cracked products from the two reactors are then mixed to form the upgraded syncrude. Using the same catalyst the two reactors may share regenerator. In a third option, the liquids produced from the vacuum resid are recycled to the flash column, so that the vacuum resid is recycled to extinction. A simplified version consists in recycling directly the resid to the main cracking reactor, where crude oil and recycle vacuum resid are cracked under the same operating conditions.

3.4.2 Silica-alumina (SA) additive. Adding silica-alumina is a common strategy in Fluid Catalytic cracking to reduce residual fraction. Used in large amounts it tends to produce increased

amounts of coke and gas, so that the amount of additive will have to be optimized.

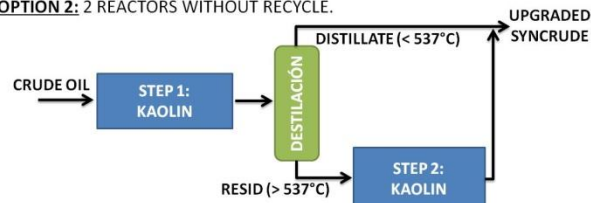
Adding 5 wt% SA to an FCC unit working in distillate mode was proven effective in reducing bottoms while maintaining coke and gas yields.¹⁴ Note that FCC base catalyst utilization was not contemplated as zeolite component would lead to an excessive cracking of the crude oil, generating excess gas (and coke) that would unnecessarily decrease the yield of liquids. Instead, bottoms cracking additive content in kaolinite inventory was varied from 5 to 25% (Table S2), and compared to pure kaolinite and SA cracking results (Figure 3).

Using 100% SA as catalyst allowed a drastic reduction of the residual content in the liquids. Although detailed properties of these liquids were not determined, the increase in gasoline fraction and the decrease of HCO fractions appoints to density and viscosities significantly lower than those obtained with kaolinite. Surprisingly the gas yield is only slightly higher using SA, which main drawback is a very high coking tendency, reducing the total liquid yield up to 20 points.

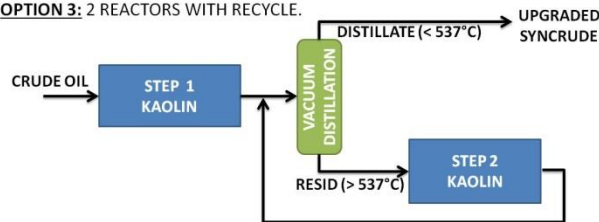
❖ OPTION 1: SINGLE REACTOR WITH BOTTOMS CRACKING ADDITIVE (SA).



❖ OPTION 2: 2 REACTORS WITHOUT RECYCLE.



❖ OPTION 3: 2 REACTORS WITH RECYCLE.



❖ OPTION 4: SINGLE REACTOR WITH RECYCLE.

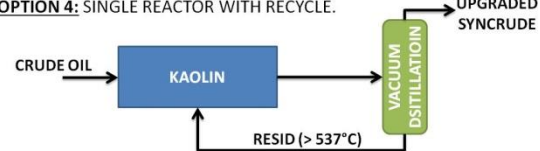


Figure 2. Different process options for obtaining a stable cracked products with minimum content in vacuum resid ($T_{eb} > 537^\circ\text{C}$)

Table 4. Cracked liquid properties from Chichimene crude oil processed in the presence of kaolin and variable amount of silica-alumina. Temperature range 530-580°C, STO 8-20, residence time 0.3 to 2 seconds

ID	10	14	18	19	20	21	22	23	24
% SA in inventory	0			5			25		
Trx (°C)	530	555	580	530	555	580	530	555	580
Residence time (s)	0,3	1,25	2,2	0,3	1.2	2,0	0,3	1.2	2,0
STO	8	12	20	8	12	20	8	12	20
Conversion (wt%)	30,9	38,2	34,2	34,0	41,4	48,4	40,0	44,2	49,2
density (15°C)	0,9385	0,9347	0,9360	0,9349	0,9338	0,9291	0,9270	0,9259	0,9219
°API	19,1	19,8	19,5	19,7	19,9	20,7	21,0	21,2	21,9
Viscosity (cst, 40°C)*	25	13	11	23	-	-	14	-	-
Metals (ppm) V	9	11	10	<1	-	-	<1	-	-
Ni	1	<1	<1	<1	-	-	<1	-	-
CCR (wt%)	2,1	3,2	4,7	2,0	2,8	3,5	1,3	2,2	2,2
n-C7 insolubles (wt%)	0,1	0,3	0,2	0,4	0,6	0,7	0,3	0,1	0,5

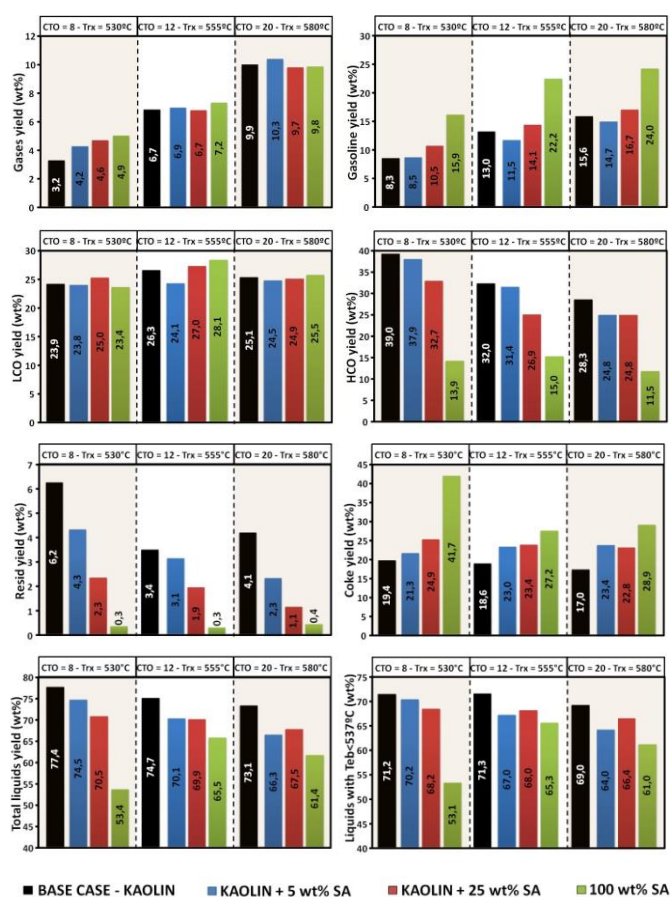


Figure 3. Yields obtained with cracking Chichimene crude oil as a function of the amount of Silica-alumina (SA) in kaolin inventory. 530-580°C temperature range. Values above bars indicate operating conditions in reactor.

As observed with kaolinite, the coke yield tends to be higher at lower temperature range, indicating desorption issues even at 530°C while such problem was mainly limited to 510°C or below with kaolinite catalyst. This is an indication that the heat

of desorption of heavy components is higher on SA than on kaolinite

Using a limited amount of SA in the kaolinite inventory mitigates the high coke yield issue. Still, with 5-25 % SA in the inventory, the coke yield increases 2-5 points respect to the base case with 100% kaolinite. Gas yield barely changes due to the low contribution from SA. Liquid yield decreases steadily upon addition of SA, while the liquid quality increases steadily, as reflected by the increasing amount of gasoline fraction, higher API and lower viscosity (Table 4). The comparison of API degree at same total liquid yield (Figure 4) indicates that the liquid quality is marginally improved in the presence of 25 wt% SA compared with the kaolinite catalyst, yet the maximum liquid yield achievable is limited to 70 wt% with such high amount of Bottoms Cracking Additive. Lower amounts of SA (5 wt%) did not result in an improvement in liquid quality compared to kaolinite. Liquids remain nearly free of metals and heptane insolubles in any case.

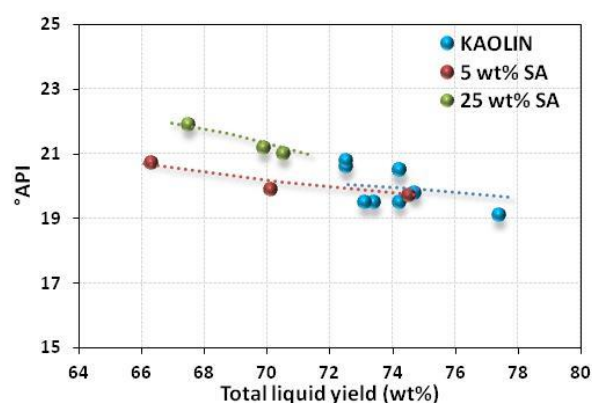


Figure 4. API degree as a function of total yield of liquid for several catalyst formulations

Finally, CCR is also lowered in the presence of moderate amounts of SA, which is certainly related to the higher coke yield. In spite of a large decrease in the residue fraction in the cracked liquids, none of these liquid products obtained with 5 or 25%wt of SA in the inventory were found stable, even with the sample produced with 25% SA at 580°C, which contained as few as 1 wt% residue (Table S3). The products obtained with SA were stable, but the loss in liquid yield is unacceptably high.

Thus, the addition of a moderate amount of SA, while improving slightly the density and viscosity of the cracked liquids, did not allow stabilizing the cracked liquids for pipeline transportation. Besides, it comes with a significant coke penalty.

3.4.4. Cracking the vacuum residue fraction from the cracked liquids in a separate reactor. The reactivity of the resid fraction with kaolinite was evaluated, in view of its elimination in a separate reactor or by recycle. For this purpose, liquids produced from several test under varying conditions were gathered, then distilled to recover the vacuum residue following ASTM D-1160 standard procedure. The SIMDIS analysis on these vacuum bottoms gave the following proportions: 0.6 wt% boiling below 359°C, 40,2 wt% boiling between 359 and 537°C, and 59,2 wt% boiling above 537°C. Its density was estimated at 1.021 g/cm³ at 20°C (API 7) by diluting with toluene and its Conradson Carbon Residue was measured at 17.3 wt%. Indeed, its properties are not very different from the crude oil before processing.

This fraction was then cracked under a range of conditions similar to those used with kaolinite material, including lowest and highest severity (Reaction temperature, residence time, STO) and a middle point. Results were summarized in Table 5.

Table 5. Cracking yields of vacuum residue of distilled from Chichimene cracked products, both feeds cracked with kaolinite. Temperature range 530-580°C, STO 8-20, residence time 0.3 to 2 seconds

ID	28	29	30
Temperature (°C)	530	555	580
Gas Residence time (s)	0,3	1,2	2,2
Solid to Oil Ratio (STO)	8	12	20
Conversion (wt%)	31,7	35,6	43,3
Gases (wt%)	3,0	6,3	8,5
- Dry Gas (H ₂ + C ₁ -C ₂)	1,5	3,4	4,7
- LPG(C ₃ -C ₄)	1,5	2,9	3,8
Liquids (wt%)	72,1	70,8	67,0
-Gasoline (C ₅ -216°C)	3,8	6,4	10,3
- LCO (216-359°C)	6,8	9,8	13,7
- HCO (359-537°C)	41,2	39,3	33,9
- Resid (>537°C)	20,3	15,3	9,1
Coke (wt%)	24,9	22,9	24,5
Cracked liquid properties			
density (15°C)	1,0084	1,0064	0,9952
°API	8,7	9,0	10,6
CCR (wt%)	10,2	11,6	11,2
n-C ₇ insolubles (wt%)	0,5	0,6	1,0

The residual fraction gave surprisingly good cracking results, not too different from the whole crude oil. Coke yield was higher, in the 23-25 wt% range, while gas yield was similar. As a consequence, liquid yield was 67-72 wt%. These ones contained less light boiling range components and more residual fraction. This last was reduced by half over the operation range, from low temperature and residence time to higher. Considering that the distillate bottoms contained 60% of resid fraction as determined from SIMDIS, the conversion of this fraction was 65-85%. If we consider that all the coke was formed from this fraction, then the coke selectivity of resid fraction can be calculated at approximately 40 wt%. The density of the cracked liquid from the vacuum resid was found significantly higher than the cracked liquids from the crude oil as a result of its composition. Conradson Carbon was also found significantly higher (10-12 wt%, Table 5), while heptane insolubles remained very low. Metals were not measured as they are already very low in the cracked liquids from which the vacuum resid was extracted.

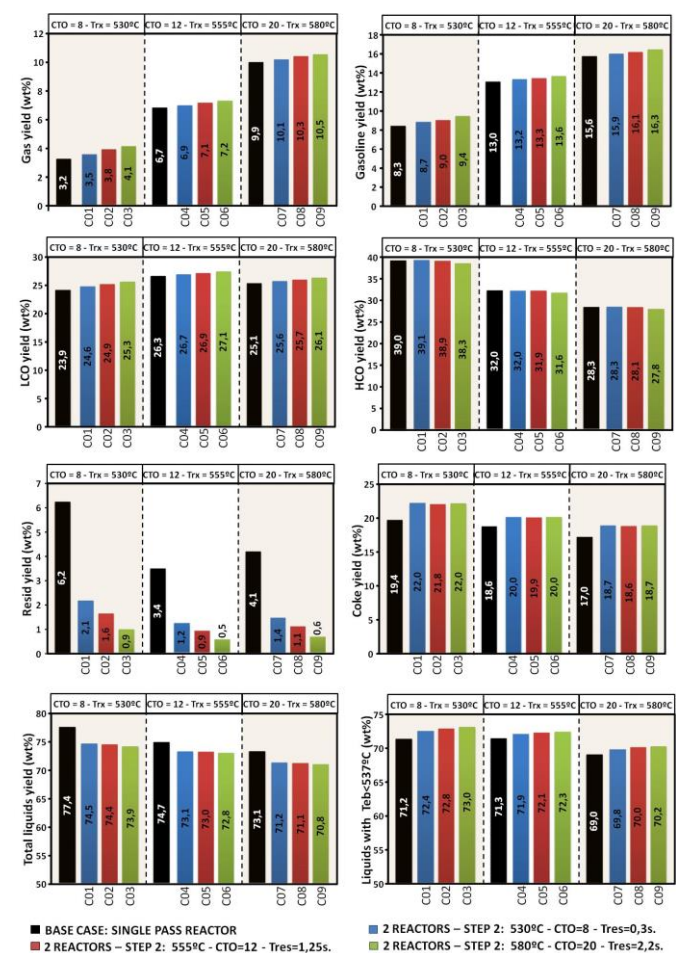


Figure 5. Combined yields output comparison between the different cracking options for two reactors processing scheme, compared with direct processing (option 2). Kaolin is used as catalyst. Values above bars indicate operating conditions in step 1

A simulation was then carried out to calculate the yield output of the two-reactor processing scheme and compare yields with single pass processing. The distillation step between first and second reactor is simulated and the amount of distillation residue is calculated, which includes the resid fraction determined by SIMDIS (60% of the distillation residue) and a 40% contribution taken from the HCO fraction also determined by SIMDIS. These are subtracted from the yields of liquids from the first reactor, and the light fraction from the first reactor is determined as in Figure S3.

The yield pattern of the distillate residue, corresponding to the elected operating conditions for the second reactor, is then applied to the amount of distillation residue determined earlier, and the output yields from the second reactor are calculated, in weight percent of the feed rate of the first reactor. The yields from the second reactor are then added to the gas, coke and distillate fraction yields obtained from the first reactor, to determine the combined yield output of the process.

Nine combinations were tested, varying cracking severity from low to high in both reactors. The summary of the operating conditions for the nine simulations are given in Table S4. Although residual fraction composition at the first reactor output may vary depending on the processing temperature, altering cracking yields in the second reactor, this first approximation served to estimate which of the options gave best liquid yield. Note that in any option we expect the density and viscosity of the oil resulting from the process to be lower than those from the single reactor process, thus compliant with pipeline transportation specifications. The results in Figure 5 shows clearly that the best combination for obtaining a maximum yield of liquids is processing the crude in a first reactor under the softer operating conditions, then cracking the residual fraction under the most severe conditions. While the processing of the crude oil under soft conditions yields more coke and residual fraction, this is more than offset by a significantly lower gas yield. Then, the residual fraction is reduced under the most severe conditions, where the increase in gas yield is more than compensated by a higher production of liquids. Under the best operating conditions, 74 wt% of liquids could be obtained with 22 wt% of coke and 4 wt% of gas. The residual fraction present in the liquids could be reduced to less than 1 wt%.

Stability of the mixed output of liquids from the combined process was evaluated experimentally combining the proper amount of liquid products from the cracking of residual fraction and from the distilled liquids from cracking of the crude oil. The stability behaviour of two mixtures corresponding to primary cracking at 530 or 580°C combined with resid processing at 580°C (lowest resid yield) are shown in Table S3. Despite having a resid content as low as 1 wt%, these mixtures were found solvent-unstable, although visual inspection showed an improvement compared to the cracked liquids from the crude oil before distillation. In order to obtain a stable lighter liquid product from the Chichimene crude, it seems then that the residual fraction in the liquids will have to be completely eliminated.

3.4.5 Recycle options. While the residual fraction of the cracked liquids could be treated in a secondary unit such a delayed coking, it would be preferable to maintain the upgrading process scheme as simple as possible, and in the same time squeeze as much liquid as possible from the residual fraction. In the former section it was demonstrated that the residual fraction was reasonably processable with kaolinite, but that it will have to be recycled to extinction for the liquids generated by the process to be stable for pipeline transportation. Thus, processing options incorporating a recycle loop were evaluated. Recycle can be carried out on a separate reactor dedicated to vacuum resid processing, or directly on the main cracking reactor.

A simulation was carried out with the data available in the former section 3.3.4, but adjusting the recycle ratio so that the resid gets fully converted in the process, as depicted in Figure S3. We are aware that the nature of some recycle residues may be different in composition and cracking activity and selectivity than the residue tested in the previous section, but this calculation will give an indication on the best strategy to follow. Note that from the point of view of calculation, when the operating conditions are the same in the two reactors (C01, C05, C09) this would be equivalent to recycling the residual fraction directly to the main reactor, without using a secondary reactor, provided the addition of recycled resid fraction do not interfere with the main cracking of the crude oil.

The results of the simulation are summarized in Figure 6. As observed in the former section, the best results are obtained by processing the crude oil under soft conditions, then the residual fraction under harsher conditions (option C03). Yet the yield shift between the different simulated options is lower in the presence of a recycle stream (option 3 and 4) than using two reactors in series (option 2). So, processing the crude oil with recycle of the residual fraction in the same reactor with no synergies (which is mathematically equivalent to C01 combination), should yield nearly as much as liquids as the best option with recycle in separate reactors, with slightly more coke and less gas due to a higher recycle ratio and lower processing conditions for the resid fraction, all this in a much simpler, single reactor process.

Based on these results an experimental confirmation was carried out following the conditions determined in C01, which is 530°C reaction temperature, short contact time of 0.3 seconds and CTO of 8 g·g⁻¹. The recycle ratio calculated to obtain residue extinction for this combination, based on real distillation data and the yields obtained in run ID10, was 15.8 wt% of the crude oil feed.

Thus, a mixture of 15.8 wt% of the vacuum residue with crude oil was prepared and cracked under the soft operating conditions (530°C, STO 8 and 0.3 s). The results are reported in Table 6 and compared to the simulated yields at the outlet of the reactor and before fractionation.

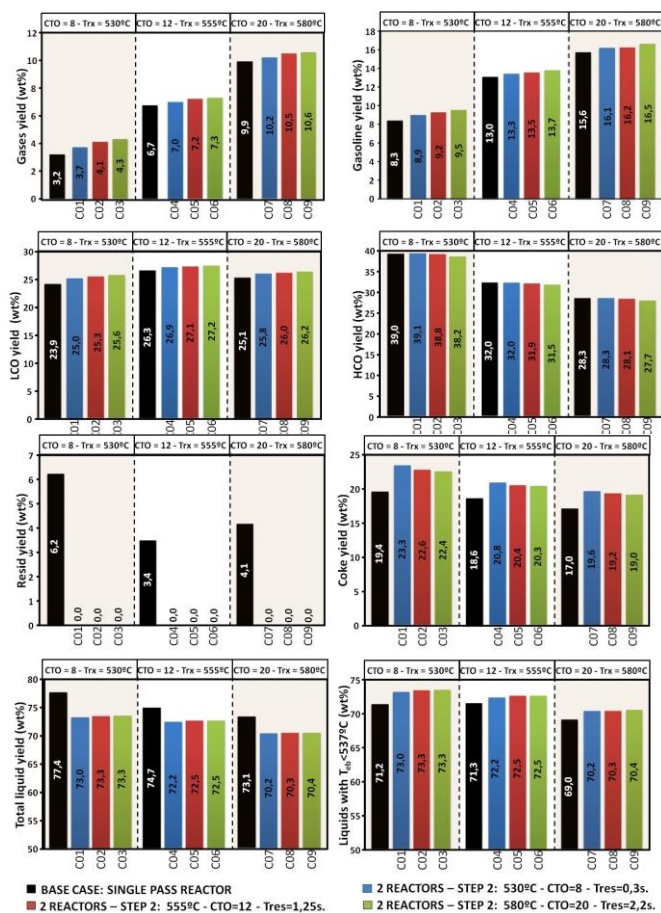


Figure 6. Simulated yields obtained in an operation with recycle and considering a configuration with two reactors. 530-580°C temperature range in the two reactors. Kaolin is used as catalyst. Values above bars indicate operating conditions in step 1.

There is very good agreement between the production and the actual experimental yield, showing actually little interaction between the cracking of the raw crude oil and the vacuum distillate from the cracked products, validating the hypothesis made for the calculation of the recycle ratio. Indeed, the amount of resid fraction obtained in Run 31 is slightly lower than expected, so that the real recycle ratio will be pretty lower than calculated. Note that the yields reported in Table 6 correspond to the normalized output from the main cracking reactor, which runs at 115.8 wt% feed rate compared to crude oil feed rate.

The cracked liquid obtained in experiment 31 was further distilled, yielding 82.1 wt% distillate and 17.9 wt% residue, very similar to the yields determined earlier with the mixture of cracked liquids from direct crude oil cracking. The distilled liquid, with a 73 wt% yield on crude oil basis, was further characterized (Table 7, Cracking column). Density was above 19 °API, and viscosity determined to be lower than 21 centistokes. The product carried less than 1 ppm of metal, and very little CCR or heptane insolubles, and was determined to be stable.

Table 6. Experimental yields from the cracking of Chichimene crude oil + vacuum distillate (16.8% of crude oil feed rate), compared to the predicted yields from separate cracking of the two feeds. 530°C, 0.3 s residence time, CTO 8

ID	31	10+28
Gases(wt%)	3,6	3,2
- Dry Gas (H ₂ + C ₁ -C ₂)	1,8	1,5
- LPG(C ₃ -C ₄)	1,8	1,7
Liquids (wt%)	76,5	76,7
-Gasoline (C ₅ -216°C)	7,2	7,7
- LCO(216-359°C)	22,0	21,4
- HCO (359-537°C)	39,5	39,3
- Resid (>537°C)	7,8	8,2
Coke (wt%)	19,9	20,3

Table 7. Process output comparison between cracking and delayed coking of Chichimene crude oil. Cracked liquid properties.

	Crude oil	Cracking	DC
Gases(wt%)	-	4,2	8,3
-Gasoline (C ₅ -216°C)	-	8,3	11,9
- LCO(216-359°C)	15	25,5	27,3
- HCO (359-537°C)	35	39,0	33,5
- Resid (>537°C)	50	0,0	0,0
Coke (wt%)	-	23,0	19,0
Total liquids	100	72,8	72,7
density (15°C)	1,0170	0,9373	0,9279
API (60°F)	7,6	19,3	21,0
Viscosity (cst., 40°C)*	-	<21	42
Metals (ppm) V	250	<1	79
Ni	82	<1	58
CCR (wt%)	17,6	0,6	2,9
n-C ₇ insolubles (wt%)	15,4	0,1	0,1

Thus, the initial crude oil that carried 50 wt% of residual fraction could be converted to a liquid approximately half Vacuum Gas Oil and half atmospheric distillates with no resid fraction, with a minor contribution to gas (4 wt%) and 23 wt% coke which represent 1.3 times the CCR of the feed.

The results of the cracking process were compared with delayed coking pilot plant data obtained with the same crude oil (Table 7). Liquid yield was similar for both processes. Gas yield was higher with delayed coking in spite of lower processing temperature due to the longer residence time of the oil in the unit (minutes vs. seconds). Gas yields up to 10 wt% are common in petroleum residue delayed coking.¹⁸ Coke yield was also surprisingly low in crude oil delayed coking, at 1.1 times Carbon Conradson Residue in the feed, while traditional values for delayed coking are generally reported at 1.5 times CCR for petroleum residue up to 25 wt% CCR, and increasing when the resid fraction is recycled to extinction.^{5,19} Such small values were reported when processing similar heavy crude oil through delayed coking.⁴

It is commonly observed in petroleum resid delayed coking that the upgraded oil retains a part of the initial oil contaminants such as metals and asphaltenes.²⁰ By the contrary, the liquid obtained from the cracking process was of higher quality, with very low CCR and complete removal of

metals. While both liquids were free of resid fraction and asphaltenes (no heptane insolubles), some CCR remained in the delayed coking liquid product, yielding a more viscous oil in spite of a lower boiling point distribution (which correlates with a lower density) than cracked oil. Nevertheless, both liquids are fully suitable for pipeline transportation without dilution. Olefin and diolefin content may be a problem due to their tendency to form gums upon prolonged storage.^{21,22} A bromine number of 43 (ASTM-D1159) and a diene number of 6 (UOP-326) were measured for the upgraded syncrude (processing option 4, Figure 2), being these values in the range found for coker liquid products. Thus, as for coking processes, the oil produced may have to be hydroprocessed for long term stability.

4. Conclusion

An Extra-heavy crude oil was processed in the presence of a kaolinite solid, yielding an upgraded liquid with low viscosity and API in the 18-20 range. The liquids were also nearly free of metals and heptane insolubles, with conversion of these contaminants above 97 %. Some Conradson Carbon remained in the products due to the presence of a reduced amount of residual fraction. All the properties of the cracked liquid were improved in the presence of kaolinite compared to pure thermal cracking, and the yield of resid-free liquids was improved 1-2 points in spite of a slightly higher coke and gas yield. The asphaltenes in the liquid produced by once-through operation were found to be unstable (modified S-value test), so that different options were examined to eliminate the residual fraction of the liquids that were responsible of this problem. Adding a Bottoms Cracking Additive was effective only at high loads, generating too much coke. Recycling of the residual fraction proved to be an effective procedure, yielding above 73 wt% of an upgraded, resid free liquid with an °API of 19.3, a viscosity below 20 centistokes at 40°C and with satisfactory asphaltene stability (Table S3). Crude oil and recycled stream were cracked in the same reactor, at 530°C, short contact time of 0.3s and CTO of 8 g·g⁻¹.

5. Acknowledgments

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