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COMPARATIVE STUDY OF THE NORMAL VISBREAKING PROCESS AND THE THERMAL FIXED-BED PROCESS APPLIED ON COLOMBIAN HEAVY OILS

*ESTUDIO COMPARATIVO DEL PROCESO DE VISCORREDUCCIÓN NORMAL
Y EL PROCESO TÉRMICO CON LECHO FIJO APLICADO
A CRUDOS PESADOS COLOMBIANOS*

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ABSTRACT

The rise in heavy oil reserves, the scarceness of light oils, the demand for clean products and the increase in residual material or bottoms make it necessary to implement or adapt technologies to process heavy oils efficiently. To this end, the modification of the current visbreaking system has been proposed, consisting of adapting a fixed bed inside the reactor in order to study possible modifications in the different thermal processes to increment and improve performance with the purpose of obtaining more valuable products from heavy oils.

This research was conducted through testing at the pilot plant level in the visbreaking unit of Ecopetrol S.A. - Instituto Colombiano del Petróleo (ICP), which provides the possibility of comparing the normal visbreaking process to the fixed-bed visbreaking process as a thermal process. Both processes are carried out in comparison to the increase in the performance of middle distillates and the quality properties of the products obtained. The comparison was completed under the same conditions of flow, flow direction (ascending), pressure, temperature and oil type.

The results revealed that the fixed-bed visbreaking process managed to convert more heavy fractions into distillates (4 to 7%) compared to the normal visbreaking process.

Keywords: Thermal cracking, Visbreaking, Delayed coking, Heavy oils, Reactors, Fixed-bed, Distillates.

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El aumento en las reservas de crudos pesados, la escasez de crudos livianos, la demanda de productos limpios y el incremento de material residual o fondos, hacen necesaria la implementación o adaptación de tecnologías que procesen crudos pesados de forma eficiente. En este sentido se plantea la modificación del esquema actual de viscorreducción adaptándole un lecho fijo dentro del reactor para estudiar posibles modificaciones en los diferentes procesos térmicos, a fin de incrementar y mejorar sus rendimientos con miras a la obtención de productos más valiosos a partir de crudos pesados.

La presente investigación se realizó mediante pruebas a nivel de planta piloto en la unidad de viscorreducción de Ecopetrol S.A. - Instituto Colombiano del Petróleo (ICP), la cual brinda la posibilidad de comparar el proceso de viscorreducción normal frente al proceso de viscorreducción con lecho fijo como proceso térmico. Ambos procesos se compararon en cuanto al incremento del rendimiento de destilados medios y propiedades de calidad de los productos obtenidos. La comparación se hizo bajo las mismas condiciones de flujo, dirección de flujo (ascendente), presión, temperatura y tipo de crudo.

Los resultados revelaron que el proceso de viscorreducción con lecho fijo logró convertir más fracciones pesadas en destilados (4 a 7%), comparado con el proceso de viscorreducción normal.

Palabras clave: Craqueo térmico, Viscorreducción, Coquización retardada, Crudos pesados, Reactores, Lecho fijo, Destilados.

O aumento nas reservas de crus pesados, a escassez de crus leves, a demanda de produtos limpos e o aumento de material residual ou fundos, fazem necessária a implantação ou adaptação de tecnologias que processem crus pesados de forma eficiente. Neste sentido é proposta a modificação do esquema atual de viscorredução adaptando-lhe um leito fixo dentro do reator para estudar possíveis modificações nos diferentes processos térmicos, com a finalidade de aumentar e melhorar seus rendimentos com vista à obtenção de produtos mais valiosos a partir de crus pesados.

A presente pesquisa foi realizada mediante provas a nível de centro piloto na unidade de viscorredução de Ecopetrol S.A. - Instituto Colombiano del Petróleo (ICP), a qual oferece a possibilidade de comparar o processo de viscorredução normal diante do processo de viscorredução com leito fixo como processo térmico. Ambos os processos são comparados em quanto ao aumento do rendimento de destilados médios e propriedades de qualidade dos produtos obtidos. A comparação foi feita sob as mesmas condições de fluxo, direção de fluxo (ascendente), pressão, temperatura e tipo de cru.

Os resultados revelaram que o processo de viscorredução com leito fixo conseguiu converter mais frações pesadas em destilados (4 a 7%), comparado com o processo de viscorredução normal.

Palavras chave: Craqueamento térmico, Viscorredução, Coqueamento retardado, Crus pesados, Reatores, Leito fixo, Destilados.

1. INTRODUCTION

The visbreaking process substantially reduces the viscosity of reduced oils and vacuum bottoms through thermal conversion, compared to other important thermal processes (Gary & Handwerk, 2001; Corredor-Rojas & Valero-Alvarado, 2004). Future developments or variations of this visbreaking process will depend on the trends in product specifications, and mainly on the types of oils available in the world, such as extra heavy oils (Pantoja, 2005). Therefore, this research analyzes a modification of the thermal visbreaking process in order to generate higher yields and more valuable products. The modification proposed herein suggests a thermal technology using heavy and extra heavy oils as raw material, which will be the only source of oil available in the future.

In doing so, this paper analyzes the effect of the presence of inert solids in the fixed bed reactor of the thermal process, in order to observe its impact and the improvement of the products in the presence thereof. In addition, it analyzes the advantages and disadvantages of this variation in the process.

The basic principle that supports the introduction of a fixed bed with inert solids in the visbreaking reactor is based on the fact that when the oil comes into contact with fixed solids in a thermal process, it leads to a more efficient, homogeneous heat transfer, thus inducing an extra thermal cracking process on the surface thereof (Bartholic & Watchung, 1979). This makes it possible for the thermal process with the fixed bed to convert more heavy fractions into light ones, thus generating much more valuable products than those generated in the normal visbreaking process.

Ivanhoe Energy (2013) has conducted previous research related to this topic, which has also studied the introduction of inert solids in the thermal cracking process. This technology is known as Heavy to Light (HTL). The HTL technological variant cracks the heavy oil thermally and converts it into a lighter fluid without the use of solvents, which facilitates the transport and use thereof by refineries (Colyar, 2010). This technology decreases the carbon from the oil through processes at high temperatures with circulating inert solids, creating

a Synthetic Crude Oil (SCO) (Ivanhoe Energy, 2013). The thermal fixed-bed process is different from the HTL process in the dynamics of the solids in the reactor and other operating conditions. Despite the difference of the two processes, their yields are comparable.

This paper compares both thermal processes under the same conditions of flow, flow direction (ascending), pressure, temperature and bottom or oil type, in order to isolate the effect caused only by inert solids on the qualities of final thermally cracked products. The operational parameters that were evaluated in the bottom products generated by both thermal processes at the same conditions were: fractions and naphtha yields, residence times and quality of products. This last aspect covers: sulfur, Conradson carbon, insolubles in n-heptane, total metals, viscosity, API gravity and stability.

2. METHODOLOGY

In order to analyze the effect of the presence of inert solids in the thermal process, 15 runs were carried out with reduced Colombian oil and 5 runs with vacuum bottoms at the visbreaking pilot plant with a capacity of 15 mL/min located at Ecopetrol S.A. - Instituto Colombiano del Petróleo (ICP).

Both the materials and the methodology used in this research are discussed in the following sections.

Materials

Reduced Oil and Vacuum Bottoms

The reduced oil and vacuum bottoms used in this research were provided by Ecopetrol S.A. All the fluids used in the experiments were generated during normal refinery operations in the first half of 2012.

The reduced oil and vacuum bottoms evaluated in this research arrived at the facilities of Ecopetrol S.A. - Instituto Colombiano del Petróleo (ICP) completely sealed. They were preserved according to the standards for storage. Table 1 illustrates the characteristics of the oils and bottoms evaluated in both processes.

Table 1. Characteristics of the oils and bottoms evaluated.

Analysis	Units	Standard	Reduced Oil A	Reduced Oil B	Reduced Oil C	Reduced Oil D	Vacuum Bottom 1	Vacuum Bottom 2
Leco sulfur	weight %	ASTM D4294-10	3.13	1.64	1.52	3	3.3	2.04
Micro carbon residue	weight %	ASTM D4530-11	23.2	17.4	14.9	33.3	32.8	28.7
P-value	-	SMS 1600 (ASTM D7060-12)	1	1.15	1.45	2.95	1.9	2.35
Merit test	-	Rodríguez, 2014	NA	NA	NA	NA	3	NA
Stability criteria	-	-	Unstable	Unstable	Stable	Stable	Stable	Stable
Insolubles in n-C7	weight %	ASTM D3279-12	20.4	16.2	9.25	20.4	31.7	22.7
Viscosity at 80°C	cP	ASTM D445-14e2	51400	2488	NA	49900	NA	ND
Viscosity at 100°C	cP	ASTM D445-14e2	7176	570	NA	6777	NA	169100
Viscosity at 120°C	cP	ASTM D445-14e2	1648	190	NA	1503	NA	17110
Calcium	mg/kg	UOP 389-14	2.11	1.38	100	2.58	2.35	3.88
Chromium	mg/kg	UOP 389-14	0.03	0.03	4.67	0.03	0.03	0.05
Iron	mg/kg	UOP 389-14	9.08	3.06	5.29	7.94	12.2	7.6
Sodium	mg/kg	UOP 389-14	4.42	3.53	10.8	1.5	2.51	7.72
Nickel	mg/kg	UOP 389-14	136	49.4	56.7	134	195	110
Vanadium	mg/kg	UOP 389-14	584	192	207	581	774	404
Aluminum	mg/kg	ASTM D5184-12	0.91	2.04	2.28	0.71	1.45	N/A
Silicon	mg/kg	ASTM D5184-12	2.47	2.4	3.35	0.63	5.65	N/A
Total metals	mg/kg	UOP 389-14	739	253	390	728	993	533
API Gravity	°API	ASTM D1250-08(2013) /ASTM D5002-13	4.8	8.8	10.6	4.2	0.3	5
Simulated distillation by fractions	Simulated distillation high temperature oils 36-740+C							

Inert Filler Material for the Fixed Bed

For quality control purposes, quartz sand was chosen as the inert filler material for the fixed bed. This material was used to ensure that the solids introduced in the visbreaking reactor were inert.

To do so, 99% purity quartz sand was acquired, whose grain surface was free from clay, with no common minerals such as ilmenite, magnetite, and with traces

(<1%) of zircon and rutile, which met the ASTM E11 - 13 quality specifications listed in Table 2.

Visbreaking Reactor

The reactor has a volume of 294.5 mL in 316 stainless steel, a diameter of 2.54 cm and a length of 60 cm. It is part of the visbreaking pilot unit of Ecopetrol S.A. - Instituto Colombiano del Petróleo (ICP) (see Figure 1).

Table 2. Characteristics of the quartz sand used in the research.

Sample of quartz sand mesh	Thermal conductivity (W/m ²)	Specific heat (kcal/kg)	Particle diameter (μm)	Dry weight (g)	Grain vol. (cm ³)	Bulk density (g/cm ³)	Grain density (g/cm ³)	Pore vol. (cm ³)	Porosity (%)	Bulk vol. (cm ³)
60-70	45.2	0.27	212-250	73.93	28.07	1.571	2.634	19	0.4036	47.06

In the case of the fixed-bed runs, a small stainless steel basket was pressure inserted to keep the inert material still during the operation. The basket was made with the same length as the isothermal zone of the reactor and then placed in the same area.

The isothermal zone had a length of 16 cm and a volume of 78.54 mL as illustrated in Figure 1. Table 3 shows the configurations of the reactor volumes for normal visbreaking and fixed-bed visbreaking.

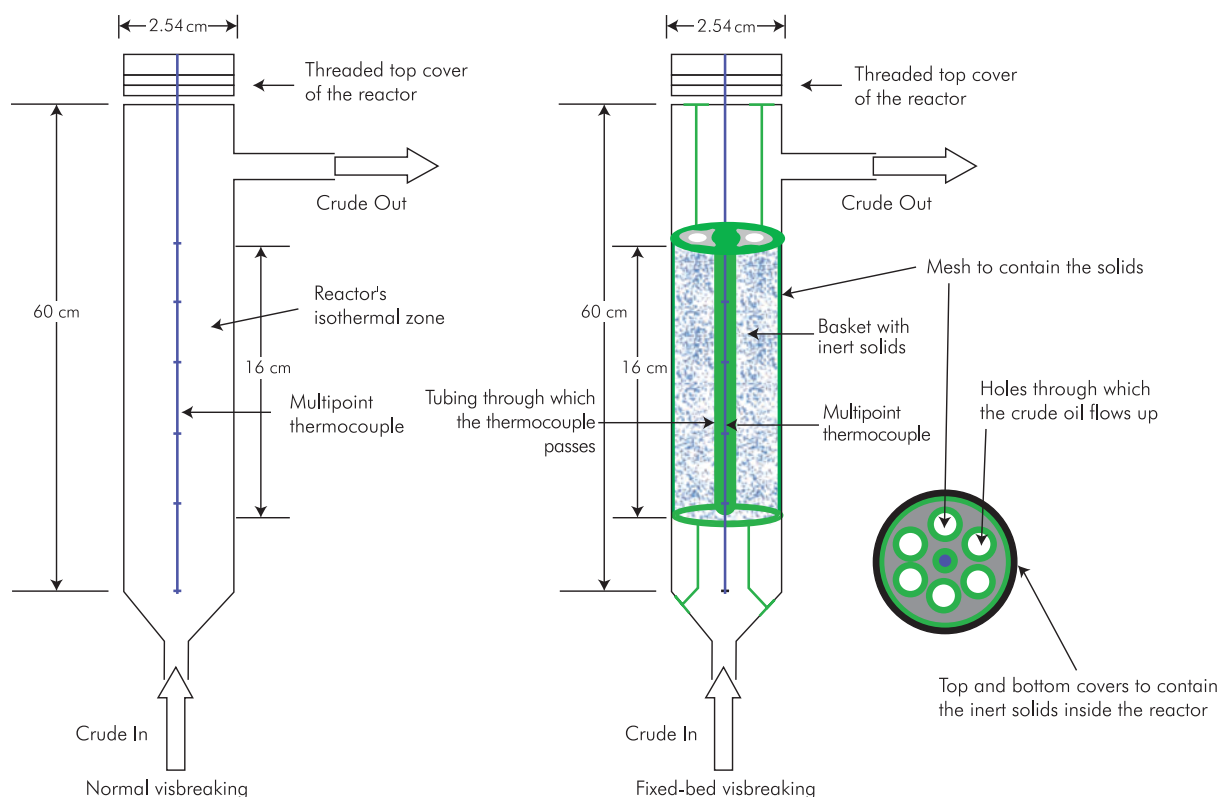


Figure 1. Normal and fixed-bed visbreaking reactor.

Table 3. Run conditions.

Operating conditions	Units	Visbreaking (without fixed-bed)	Visbreaking (with fixed-bed)
Void volume of the reactor	mL	294.52	245.52
Void volume of the isothermal zone	mL	78.54	29.54
Volume of sand added	mL	NA	49
Sand density	g/mL	NA	1.407
Sand mass added	g	NA	69
Residence time in isothermal zone	min	2.23-2.41	0.84-0.88
Space velocity	min ⁻¹	0.44-0.41	1.19-1.13
Reaction temperature	°C	450-530	450-530

In each run, the basket was loaded with clean inert solids, then closed and the pressure inserted in the isothermal zone of the reactor.

All the experiments were conducted with ascending flow to mitigate liquid distribution problems that arise in fixed-bed reactors with descending flow, such as channeling (Fogler, 1979; Smith, 1991; Froment & Bischoff, 1979; Iborra, Tejero & Cunill, 2013; Levenspiel, 1999).

In addition, the reactor is installed in the furnace and programmed at different operating conditions for each run.

Flowchart of the Visbreaking Pilot Unit

The unit included a feed section, with preheating and a feed pump; a reaction section, which includes the reactor and furnace; a separation section, which includes a separator and condenser, and finally, the gas collection and measurement system (see Figure 2).

Methodology

The following section describes the methodology used in the evaluation of normal and fixed-bed visbreaking processes.

Evaluation Runs in Pilot Plants

For both processes, the mass and pressure flow parameters were kept constant at 35 g/min and 14.7

psia respectively. All other conditions of the runs are listed in Table 3.

Technical Procedure at the Pilot unit

The procedure followed was established for the visbreaking pilot unit. The variation in the process was the installation of the fixed-bed system.

The steps below were followed:

- Runs with fixed bed: Introduction of inert solids in the basket installed inside the visbreaking reactor.
- Stabilization of reactor temperature.
- Temperature ramp scheduled to increase furnace temperature gradually up to the specific reaction temperature.
- Stabilization of reaction temperature in the reactor.
- Start of the actual run at programmed conditions.
- End of the actual run.
- Collection of products of the actual run and quantification thereof.
- Mass balances of the run.

The runs were carried out in duplicate to ensure repeatability in the data.

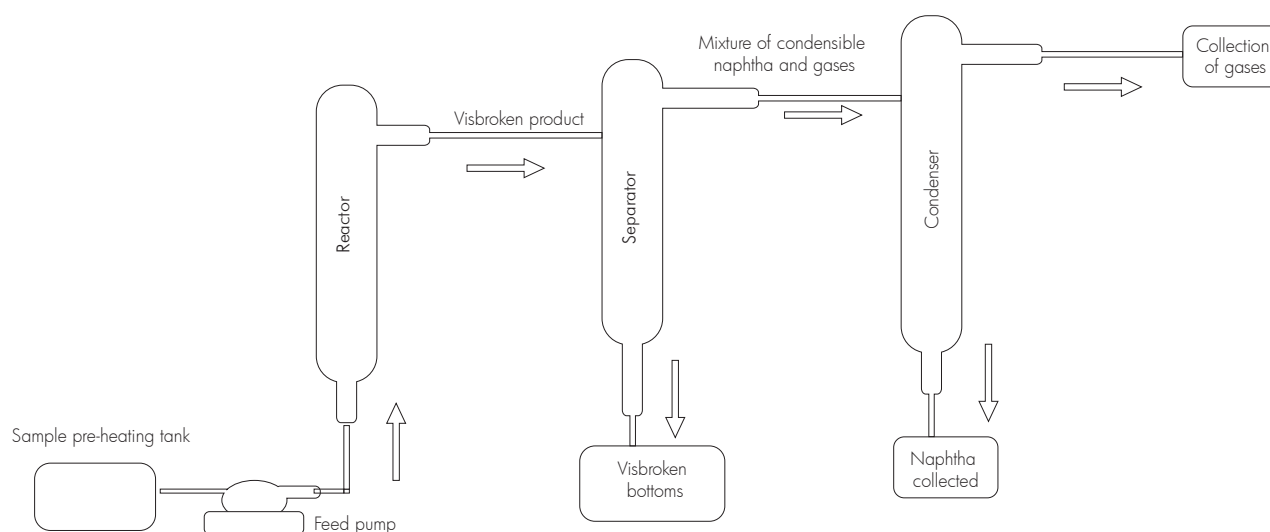


Figure 2. Flowchart of the visbreaking pilot unit.

3. RESULTS

The different results are shown by type of feed and each type of process evaluated.

Reduced Oil A

Table 4 shows the operating conditions with the results of the mass balances and physical chemical properties in the normal visbreaking processes and the thermal fixed-bed process for Reduced Oil A. Replicas were carried out for most of them with good reproducibility results; however, due to their physical

chemical properties, some oils could not be evaluated using the same characteristics of the product.

Yield by Distilled Fractions

Figure 3 shows the different fractions obtained in the normal visbreaking and thermal fixed-bed processes using Reduced Oil A.

Percentage Recovered at 460°C and Naphtha Yields

Figure 4 shows the results of the percentages recovered at 460°C and the naphtha yields of the normal visbreaking process and the thermal fixed-bed process using Reduced Oil A.

Table 4. Overall results for Reduced Oil A.

Data analyzed		Type of process		
		Visbreaking	Fixed-bed	Fixed-bed
Residence time in isothermal zone (min)		2.3	0.9	0.9
Reaction temperature (°C)		500	450	500
Flow (g/min)		35	35	35
Pressure (psia)		14.7	14.7	14.7
Total run time (min)		60	90	60
Micro carbon residue (weight %)		25.7	23.8	25.1
Insolubles in n-C7 (weight %)		22.6	23	25.3
P-value		-	1.5	1.3
Merit test		7.0	-	-
Type of stability		Stable	Stable	Stable
Viscosity at 80°C (cP)		8735	6480	10970
Viscosity at 100°C (cP)		1524	1234	2075
Viscosity at 120°C (cP)		419	357	558
Total metals (mg/kg)		723.4	712.7	836.4
Net Balance	% Gas	0.01	4.72	0.09
	% Naphtha	4.82	3.96	16.63
	% Heavier distillates	97.54	89.48	82.61
	% Coke	0.04	0.16	0.50
	% Total	102.4	98.3	99.8

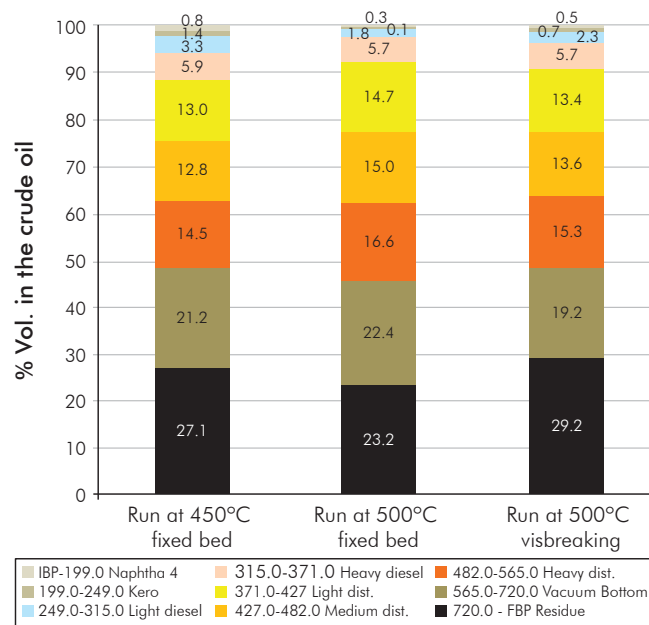


Figure 3. Fractions obtained in normal visbreaking and the thermal fixed-bed process - Reduced Oil A.

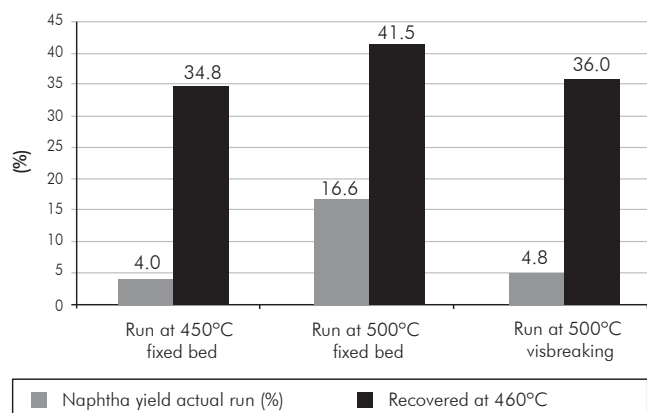


Figure 4. Percentage recovered at 460°C and naphtha yields by type of process - Reduced Oil A.

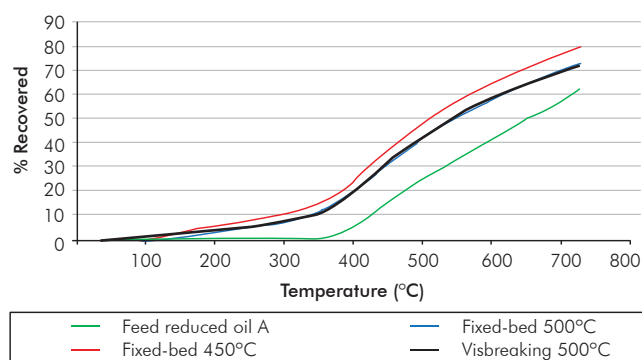


Figure 5. Composite product curves by type of process - Reduced Oil A.

Curves of the Product Recovery Percentage

Figure 5 shows the product recovery percentage curves for the normal visbreaking and thermal fixed-bed processes using Reduced Oil A.

Reduced Oil B

Overall Results

Table 5 shows the operating conditions with results of the mass balances and physical chemical properties in the normal visbreaking and thermal fixed-bed processes for Reduced Oil B.

Yield by Distilled Fractions

Figure 6 shows the different fractions obtained in the normal visbreaking and thermal fixed-bed processes using Reduced Oil B.

Percentage Recovered at 460°C and Naphtha Yields

Figure 7 shows the results of the percentages recovered at 460°C and the naphtha yields of the normal visbreaking and the thermal fixed-bed processes using Reduced Oil B.

Table 5. Overall results for Reduced Oil B.

Data analyzed	Type of process		
	Visbreaking	Fixed-bed	Fixed-bed
Residence time in isothermal zone (min)	2.26	0.85	0.85
Reaction temperature (°C)	500	450	500
Flow (g/min)	35	35	35
Pressure (psia)	14.7	14.7	14.7
Total run time (min)	60	60	50
Micro carbon residue (weight %)	17.8	18.4	18.56
Insolubles in n-C7 (weight %)	14	16.62	16.21
P-value	-	1.05	1.05
Merit test	8.50	-	-
Type of stability	Unstable	Unstable	Unstable
Viscosity at 80°C (cP)	392	6 665	681
Viscosity at 100°C (cP)	141	514	217
Viscosity at 120°C (cP)	67.37	165	90
Total metals (mg/kg)	200.2	246.2	226.3
Net Balance	% Gas	0.03	14.50
	% Naphtha	5.81	2.43
	% Heavier distillates	91.29	83.86
	% Coke	0.94	0.43
	% Total	98	101.2

Curves of the Product Recovery Percentage

Figure 8 shows the product recovery percentage curves for the normal visbreaking and thermal fixed-bed processes using Reduced Oil B.

Reduced Oil C

Overall Results

Table 6 shows the operating conditions with results of the mass balances and physical chemical properties in the normal visbreaking and thermal fixed-bed processes for Reduced Oil C.

Yield by Distilled Fractions

Figure 9 shows the different fractions obtained in the normal visbreaking and thermal fixed-bed processes using Reduced Oil C.

Percentage Recovered at 460°C and Naphtha Yields

Figure 10 shows the results of the percentages recovered at 460°C and the naphtha yields of the normal visbreaking and the thermal fixed-bed processes using Reduced Oil C.

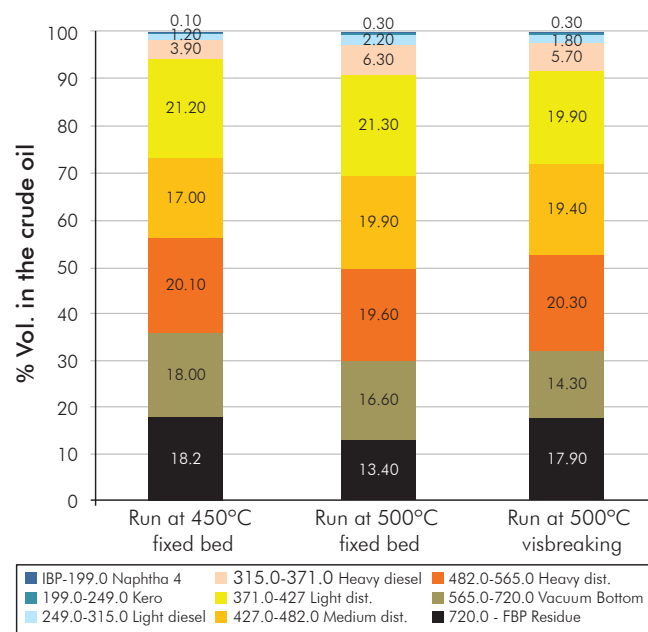


Figure 6. Fractions obtained in normal visbreaking and the thermal fixed-bed process - Reduced Oil B.

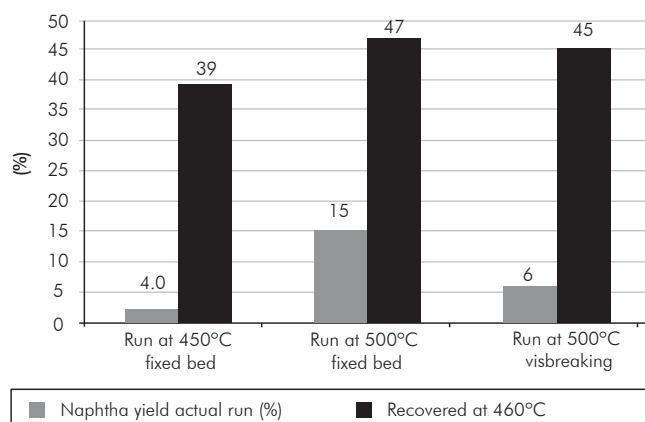


Figure 7. Percentage recovered at 460°C and naphtha yields by type of process - Reduced Oil B.

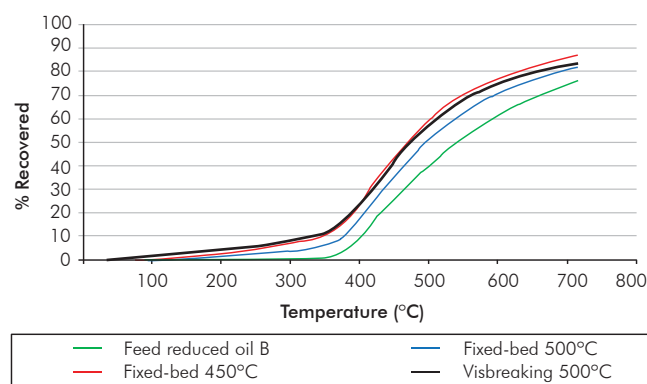


Figure 8. Composite product curves by type of process - Reduced Oil B.

Curves of the Product Recovery Percentage

Figure 11 shows the composite product curves for the normal visbreaking and thermal fixed-bed processes using Reduced Oil C.

Reduced Oil D

Overall Results

Table 7 shows the operating conditions with results of the mass balances and physical chemical properties in the normal visbreaking and thermal fixed-bed processes for Reduced Oil D.

Yield by Distilled Fractions

Figure 12 shows the different fractions obtained in the normal visbreaking and thermal fixed-bed processes using Reduced Oil D.

Percentage Recovered at 460°C and Naphtha Yields

Figure 13 shows the results of the percentages recovered at 460°C and the naphtha yields of the normal visbreaking and the thermal fixed-bed processes using Reduced Oil D.

Table 6. Overall results for Reduced Oil C.

Data analyzed	Type of process				
	Visbreaking	Fixed-bed	Fixed-bed	Fixed-bed	Fixed-bed
Residence time in isothermal zone (min)	2.23	0.84	0.84	0.84	0.84
Reaction temperature (°C)	508	450	450	500	500
Flow (g/min)	35	35	35	35	35
Pressure (psia)	14.7	50	50	14.7	14.7
Total run time (min)	60	50	60	60	60
Micro carbon residue (weight %)	15.8	14.2	15.9	16.0	16.0
Insolubles in n-C7 (weight %)	8.6	11.6	13.0	12.4	12.4
P-value	-	1.05	1.05	1.05	1.05
Merit test	9	-	-	-	-
Type of stability	Unstable	Unstable	Unstable	Unstable	Unstable
Viscosity at 80°C (cP)	92	249	275	247	170
Viscosity at 100°C (cP)	37.70	87.66	100.00	88	69
Viscosity at 120°C (cP)	19.45	39.86	46.08	43.91	35.59
Total metals (mg/kg)	179.46	266.71	280.15	260.68	225.46
Net Balance	% Gas	3.37	0.05	21.05	11.34
	% Heavier distillates	82.4	87.1	78.3	81.3
	% Naphtha	6.82	0.93	3.31	5.96
	% Coke	5.48	0.16	0.14	0.29
	% Total	98.0	88.2	102.8	102.7

Composite Product Curves

Figure 14 shows the product recovery percentage curves for the normal visbreaking and thermal fixed-bed processes using Reduced Oil D.

Vacuum Bottom 1

Overall Results

Table 8 shows the operating conditions with results of the mass balances and physical chemical properties in the normal visbreaking and thermal fixed-bed processes for Vacuum Bottom 1.

Yield by Distilled Fractions

Figure 15 shows the different fractions obtained in the normal visbreaking and thermal fixed-bed processes using Vacuum Bottom 1.

Percentage Recovered at 460°C and Naphtha Yields

Figure 16 shows the results of the percentages recovered at 460°C and the naphtha yields of the normal visbreaking and the thermal fixed-bed processes using Vacuum Bottom 1.

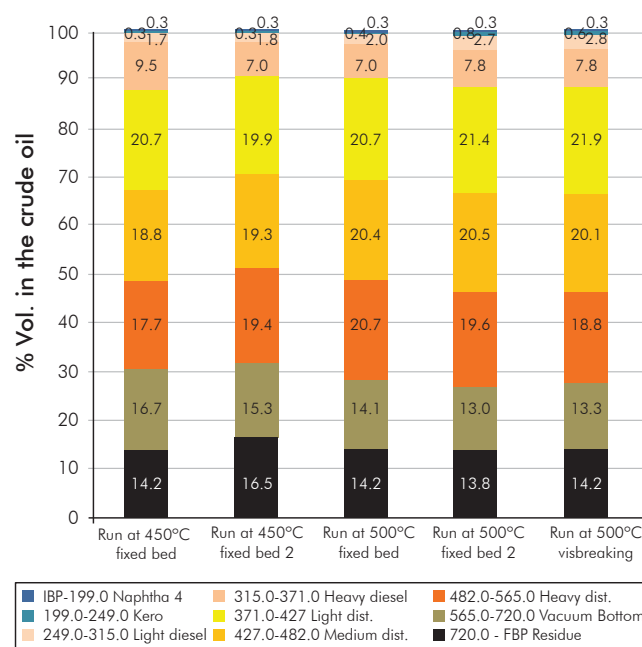


Figure 9. Fractions obtained in normal visbreaking and the thermal fixed-bed process - Reduced Oil C.

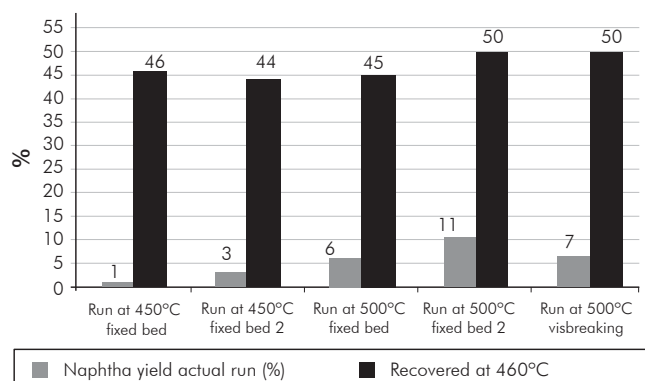


Figure 10. Percentage recovered at 460°C and naphtha yields by type of process - Reduced Oil C.

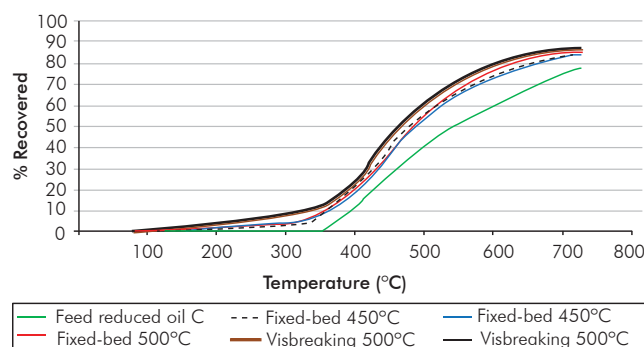


Figure 11. Composite product curves by type of process - Reduced Oil C.

Composite Product Curves

Figure 17 shows the composite product curves for the normal visbreaking and thermal fixed-bed processes using Vacuum Bottom 1.

Vacuum Bottom 2

Overall Results

Table 9 shows the operating conditions with results of the mass balances and physical chemical properties in the normal visbreaking and thermal fixed-bed processes for Vacuum Bottom 2.

Yield by Distilled Fractions

Figure 18 shows the different Fractions obtained in the normal visbreaking and thermal fixed-bed processes using Vacuum Bottom 2.

Percentage Recovered at 460°C and Naphtha Yields

Figure 19 shows the results of the percentages recovered at 460°C and the naphtha yields of the normal visbreaking and the thermal fixed-bed processes using Vacuum Bottom 2. In the experimental design, the temperature of 460°C was chosen to assess the yield percentage on a general level.

Table 7. Overall results for Reduced Oil D.

Data analyzed	Type of process			
	Visbreaking	Fixed-bed	Fixed-bed	Fixed-bed
Residence time in isothermal zone (min)	2.34	0.88	0.88	0.88
Reaction temperature (°C)	500	450	450	500
Flow (g/min)	35	35	35	35
Pressure (psia)	14.7	14.7	14.7	14.7
Total run time (min)	60	40	40	50
Micro carbon residue (weight %)	25.3	16.3	16.8	24.9
Insolubles in n-C7 (weight %)	23.60	13.88	15.10	23.50
P-value	-	1.05	1.10	1.15
Merit test	8.50	-	-	-
Type of stability	Unstable	Unstable	Unstable	Unstable
Viscosity at 80°C (cP)	18 070	164	327	6881
Viscosity at 100°C (cP)	2 301	63	103	1777
Viscosity at 120°C (cP)	548	30.7	44.1	319.0
Total metals (mg/kg)	642.9	367.8	366.9	721.0
Net Balance	% Gas	0.03	1.41	15.49
	% Naphtha	4.74	2.98	3.10
	% Heavier distillates	93.9	88.3	84.7
	% Coke	0.90	4.30	2.91
	% Total	99.5	97.0	106.2

Curves of the Product Recovery Percentage

Figure 20 shows the product recovery percentage curves for the normal visbreaking and thermal fixed-bed processes using Vacuum Bottom 2.

4. DISCUSSION

It is important to clarify that due to the physical chemical conditions of the oils, the operational unit could not be taken to the same conditions proposed in the experimental design. This has generated recommendations for improvement in future studies at the pilot plant.

Yield by Distilled Fractions

Reduced Oils

In the thermal fixed-bed and normal visbreaking processes assessed in operating ranges (see Figures 3, 6, 9 and 12), it has been shown that the fixed-bed process has a higher conversion of heavy to medium fraction quantities in comparison with the normal visbreaking process (without fixed-bed).

There was large-scale production of heavy distillates for both processes, but when comparing the results between the thermal fixed-bed process and the normal

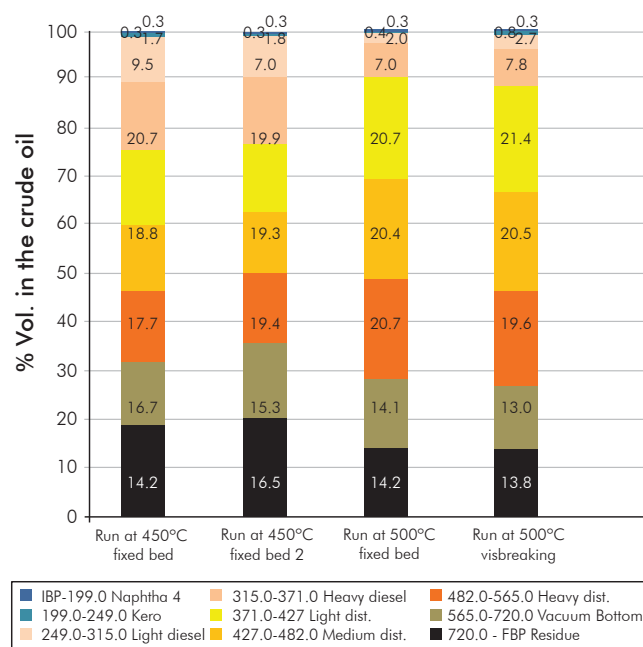


Figure 12. Fractions obtained in normal visbreaking and the thermal fixed-bed process - Reduced Oil D.

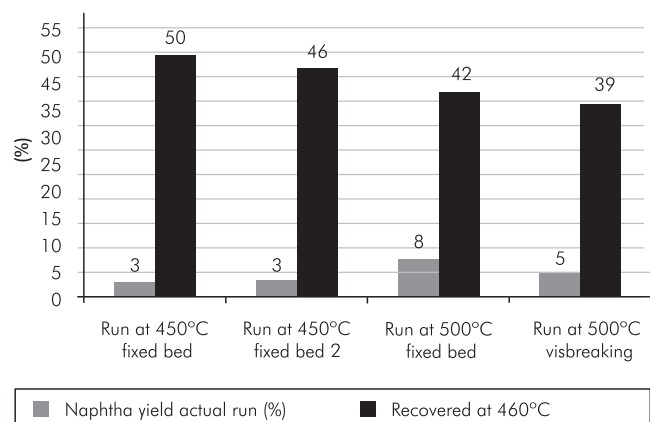


Figure 13. Percentage recovered at 460°C and naphtha yields by type of process - Reduced Oil D.

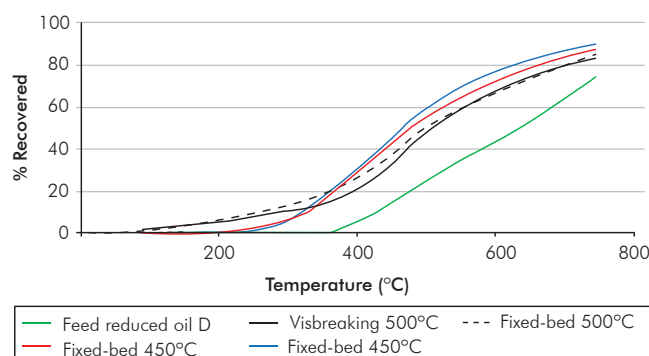


Figure 14. Composite product curves by type of process - Reduced Oil D.

visbreaking process in the same conditions, the thermal fixed-bed process shows a better yield of medium fractions (see Table 10).

Vacuum Bottoms

In the case of vacuum bottoms, the tendency described is the same for reduced oils, but a little more marked (see Figures 17 and 18) because there is a higher conversion of heavy to medium fractions in the products of the process with the fixed-bed.

This tendency to convert more heavy fractions to light fractions in the thermal fixed-bed process is thought to occur because there is a tendency for heavy fractions circulating upwards and colliding with the inert solids in the reactor to undergo additional thermal cracking on the surfaces of the inert solids fixed on the bed (Bartholic & Watchung, 1979).

The deposition of heavy fractions on the surface of the inert solids is due to a coalescence of liquid droplets on the solid, adsorption, condensation or a combination

Table 8. Overall results for Vacuum Bottom 1.

Data analyzed		Type of process		
		Visbreaking	Fixed-bed	Fixed-bed
Residence time in isothermal zone (min)		2.32	0.87	0.87
Reaction temperature (°C)		500	450	500
Flow (g/min)		35	35	35
Pressure (psia)		15	15	15
Total run time (min)		35	30	30
Micro carbon residue (weight %)		28.5	26.3	36.9
Insolubles in n-C7 (weight %)		26.2	23.5	31.3
P-value		-	1.60	1.25
Merit test		8	-	ND
Type of stability		Unstable	Stable	-
Viscosity at 80°C (cP)		275100	2350	-
Viscosity at 100°C (cP)		39400	622	-
Viscosity at 120°C (cP)		4 515	292	19 929
Total metals (mg/kg)		524.5	484.9	598.4
Net Balance	% Gas	4.83	11.98	2.58
	% Naphtha	5.79	13.61	32.03
	% Heavier distillates	80.25	49.70	61.01
	% Coke	9.09	1.78	4.43
	% Total	100.0	77.1	100.1

of these mechanisms. This takes place because the heavy fractions are in the liquid oil phase due to high boiling points and not in the vapor phase of the same oil that goes through the same bed (Bartholic & Watchung, 1979).

In addition to the above, in previous studies in which inert solids were added to thermal processes, it was clearly shown that the activation energies for the reactions involved when carrying out thermal cracking with inert solids are lower than when thermal cracking is carried out only on oil (Phillips, Haidar & Poon,

1985). The drop in activation energies when there are inert solids present may be due to the following mechanism:

- A catalytic step at the beginning of the reaction, in which the inert solids "act" as catalysts (Phillips *et al.*, 1985).
- A thermal step in which the particles of inert solids lose their catalytic activity as they are wrapped in a layer of coke (Phillips *et al.*, 1985).

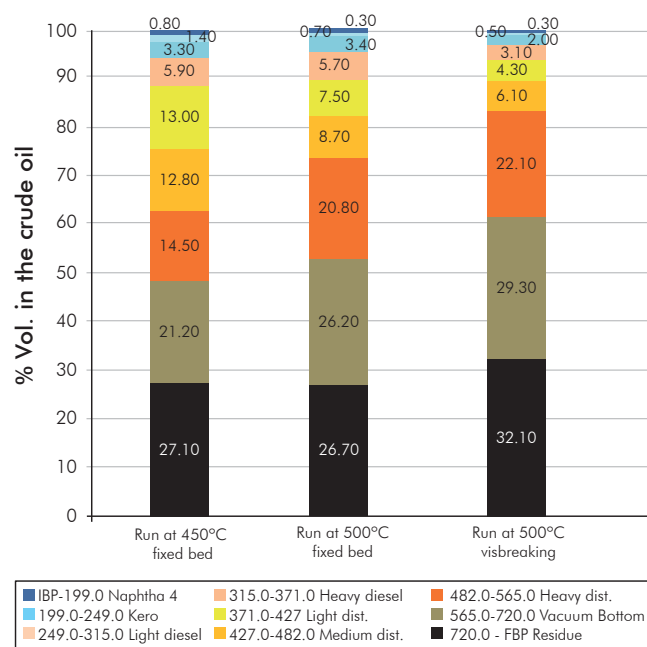


Figure 15. Fractions obtained in normal visbreaking and the thermal fixed-bed process - Vacuum Bottom 1.

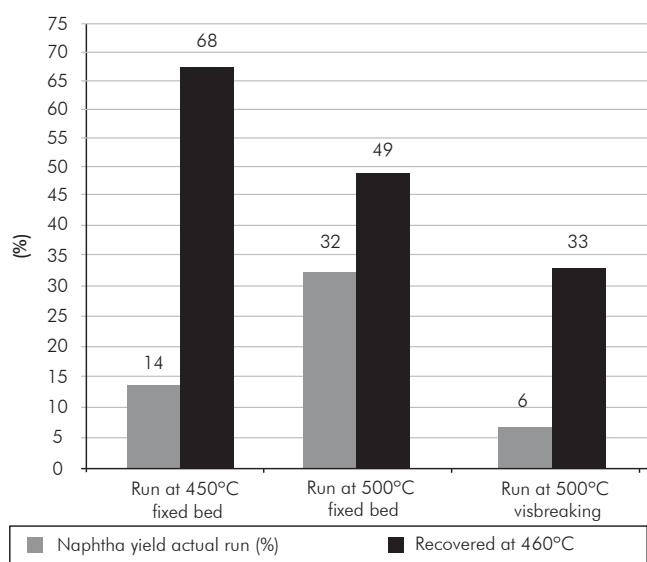


Figure 16. Percentage recovered at 460°C and naphtha yields by type of process - Vacuum Bottom 1.

A low activation energy is expected in the catalytic step, and the activation of the reaction is average. According to Phillips *et al.* (1985), while the activation energy values remain in the thermal cracking region, it can be assumed that the catalytic step is small compared to the thermal step. Alternately, the effect of the inert solids is merely physical, increasing the surface area of the reaction zone and preventing the cracked molecules

from leaving the reaction zone, which increases the probability of bimolecular reactions and, therefore, additional cracking on the surfaces of the inert solids (Phillips *et al.*, 1985). As a result, there is a further increase in the conversion of heavy fractions to light fractions.

The values of activation energy for thermal cracking without inert solids range from 170 to 300 kJ/mol, while the values with inert solids range from 24.3 to 56.9 kJ/mol. (Phillips *et al.*, 1985).

The phenomenon described above makes the thermal fixed-bed process provide a higher conversion

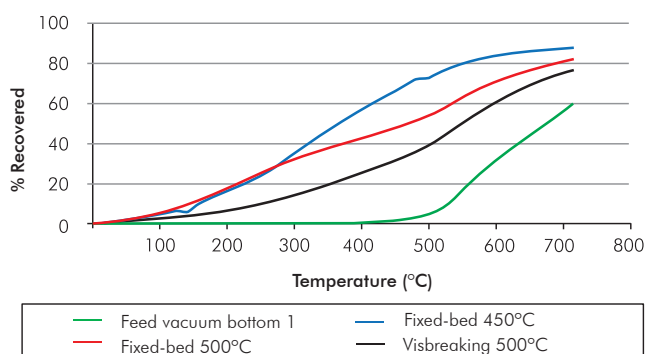


Figure 17. Composite product curves by type of process - Vacuum Bottom 1.

Table 9. Overall results for Vacuum Bottom 2.

Data analyzed	Type of process	
	Visbreaking	Fixed-bed
Residence time in isothermal zone (min)	2.41	0.91
Reaction temperature (°C)	500	500
Flow (g/min)	35	35
Pressure (psia)	14.7	14.7
Total run time (min)	80	40
Micro carbon residue (weight %)		42.2
Insolubles in n-C7 (weight %)	48.3	41.95
Merit test	8	
Type of stability	Unstable	
Viscosity at 210°C (cP)	565	
Total metals (mg/kg)	1320	1228
Net Balance	% Gas	0.04
	% Naphtha	12.36
	% Heavier distillates	76.30
	% Coke	0.62
	% Total	89.32

than that of the normal visbreaking process at the same temperature.

Table 10 shows the additional yields obtained in the thermal fixed-bed process compared to the normal visbreaking process.

Table 10. Average percentages of conversion from heavy to medium fractions.

Averages	
Average in reduced oils	+3.40%
Average in vacuum bottoms	+6.00%
Overall arithmetic average	+4.70%

Residence Times, Naphtha Yield and Percentage recovered at 460°C

Reduced Oils

Residence Times: In the fixed-bed thermal process, residence time is reduced due to the introduction of a fixed bed in the reactor. This aspect caused the thermal fixed-bed process -although the same reactor was used for both processes- to have less void volume in order for the oil to flow through the reactor. This caused the residence times in the thermal fixed-bed process to be lower than in the normal visbreaking process, although both processes handled the same mass flows (see Tables 4, 5, 6 and 7).

This provided the thermal fixed-bed process with an oil space velocity greater than that of the normal visbreaking process.

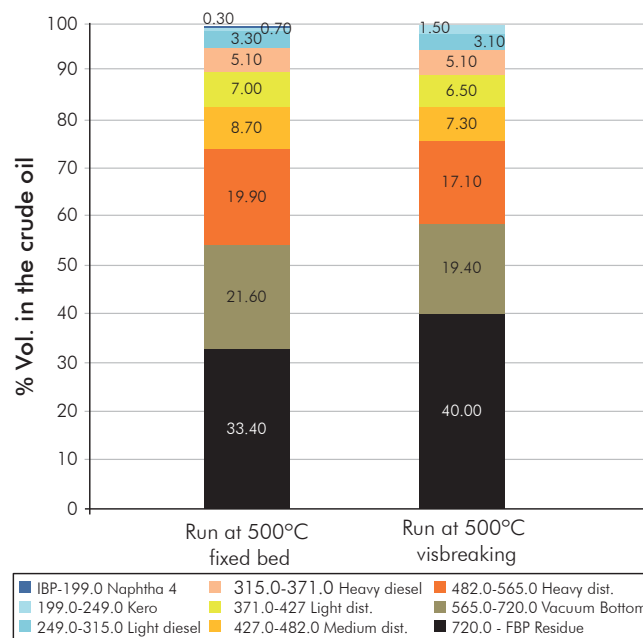


Figure 18. Fractions obtained in normal visbreaking and the thermal fixed-bed process - Vacuum Bottom 2.

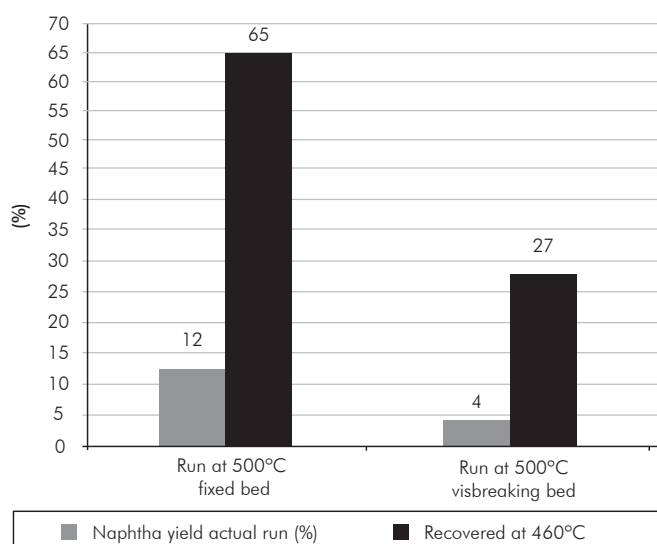


Figure 19. Percentage recovered at 460°C and naphtha yields by type of process - Vacuum Bottom 2.

Naphtha Yields: As you can see in Figures 4, 7, 10 and 12, the thermal fixed-bed process has higher naphtha yields compared to the normal visbreaking process at the same process conditions. This is explained with the same principles that described the Yield by Distilled Fractions section. The higher quantities of naphthas collected during the thermal fixed-bed process are supported by the additional thermal cracking suffered by

the surfaces of the inert solids in the thermal fixed-bed process, which did not occur in the normal visbreaking process.

The additional thermal cracking on the surfaces of the inert solids is also thought to occur due to the thermal micro-activity present in the inert solids, which leads to greater naphtha production in the thermal fixed-bed process.

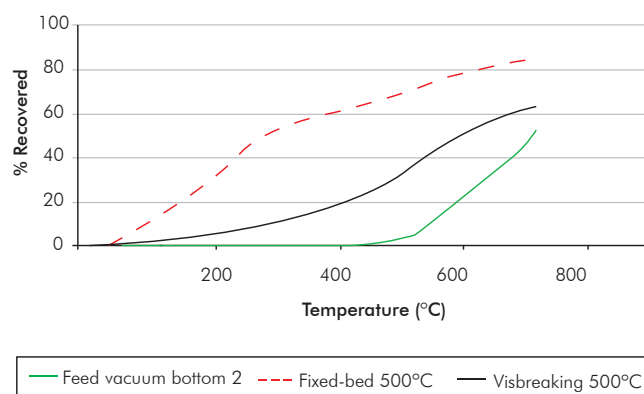


Figure 20. Composite product curves by type of process - Vacuum Bottom 2.

Percentage Recovered for Gas Oils (+460°C): The thermal fixed-bed process shows a tendency to produce more yields in fractions of +460°C than the normal visbreaking process (see Figures 4, 7, 10 and 12). This is explained with the same principles discussed in the Yield by Distilled Fractions and Residence Times, Naphtha Yield and Percentage Recovered at 460°C sections.

Based on these principles, the presence of inert solids in the thermal fixed-bed process leads to higher yields than the normal visbreaking process for fractions of +460°C.

These volumetric quantities of additional light fractions detected at 460°C in the thermal fixed-bed process are not detected in the normal visbreaking process because they remained in the heavy uncracked fractions.

The fractions that were not cracked in the normal visbreaking process appear as heavy fractions and, therefore, contributed to the greater yield of heavy fractions, which are distilled at higher temperatures (>460°C).

Vacuum Bottoms

In the case of vacuum bottoms, the tendency described is the same for reduced oils, but a little more marked (see Tables 8 and 9 and Figures 16 and 19) because there is a higher conversion of heavy to medium fractions in the products of the thermal fixed-bed process.

Curves by Distilled Fractions

Reduced Oil

Figure 5 shows that there are higher percentages of recovered products (between 4 and 5%) in the thermal fixed-bed process at cutting temperatures greater than approximately 300°C for Reduced Oil A.

In the case of Reduced Oil B, it shows that there are higher percentages of recovered products (between 1 and 2%) in the thermal fixed-bed process at cutting temperatures greater than approximately 460°C (See Figure 8).

In the case of Reduced Oil C, it shows that there are similar percentages of recovered products (+/- 1%) at

cutting temperatures greater than approximately 300°C (See Figure 11).

In the case of Reduced Oil D, it shows that there are higher percentages of recovered products (between 8 and 10%) in the thermal fixed-bed process at cutting temperatures greater than approximately 300°C (See Figure 14).

This indicates that there are more medium fractions detected much quicker in the thermal fixed-bed process, than in the normal visbreaking process.

Regarding the total percentage recovered, both processes have similar results because the presence of inert solids only "converts" or "turns" heavy fractions into light ones. The presence of inert solids, which turns heavy fractions into light ones, does not affect the global mass balance of the process; it only "converts" or "transforms" heavy fractions into light ones internally, within the liquid products.

Vacuum Bottoms

There was an even greater difference with vacuum bottoms due to the larger quantity of heavy fractions in them, that were turned into light ones during the thermal fixed-bed process. The boiling point curves of the thermal fixed-bed process show higher percentages of recovery at more temperatures than the normal visbreaking process, thus indicating a greater conversion of heavy fractions to light ones (approximately 20%) (See Figures 17 and 20).

Product Quality Property

Conradson Micro Carbon Residue

It is well known that Conradson micro carbon is a measurement used to determine oil's tendency to form carbon deposits during the evaporation thereof. Therefore, the effect of higher Conradson carbon is the increase in the portion of the feed turned into "coke", which - in this case - is deposited on the inert solid or internal surfaces of the reactor.

In addition, it is well known that the coke and metals in oil tend to concentrate in the heavy fractions because most of them have a high boiling point. These fractions, containing metals, among other things, nickel and

vanadium, are powerful catalysts for the production of coke and hydrogen.

Below are the Discussions

Reduced Oil: In all the oils analyzed in the normal visbreaking process and the thermal fixed-bed process, there was an increase in the values of Conradson micro carbon with respect to the feed (see Tables 4, 5, 6 and 7). In addition, the values of Conradson micro carbon of the visbroken products in the thermal fixed-bed process were greater than the values found in the normal visbreaking process. This suggests that it is due to the fact that the inert solids in the thermal fixed-bed process turn more heavy fractions into light fractions (greater conversion rate), "concentrating" the polyaromatic molecules even more in the remaining heavy fractions in the visbroken product of the thermal fixed-bed process, which are the precursors of Conradson Micro Carbon. This is confirmed by the higher yield of naphthas obtained in the thermal fixed-bed process mentioned in the Residence Times, Naphtha Yield and Percentage Recovered at 460°C and Curves by Distilled Fractions sections.

Vacuum Bottoms: The effect on vacuum bottoms is much more marked than for reduced oils. This is explained by the fact that the vacuum bottoms contain larger quantities of heavy fractions (see Tables 8 and 9).

API Gravity, P-Value and Viscosity

The following tendencies were observed in the reduced oils and vacuum bottoms that were processed:

- Both processes have a significant reduction in viscosity with respect to the feed; however, comparing the two processes analyzed in this research, there were no significant differences between them.
- Both processes have a significant increase in API gravity with respect to the feed; however, there were no significant differences between the two processes analyzed.
- As regards the property of stability by P-Value or merit test, it was observed that they are within the limits of stability established as parameters of quality, showing tendencies toward unstable products.

5. CONCLUSIONS

- The thermal fixed-bed process is presented as a process for the enhancement of heavy crudes without using diluent and by means of which higher yields (approximately 5%) are obtained from more valuable products (middle distillates) compared to the normal visbreaking process. This percentage varies (+/-3) depending on the type of oil.
- The presence of inert solids in the thermal fixed-bed process helps to convert more heavy fractions into medium fractions than the normal visbreaking process. Regarding the reduced oils that were evaluated, increases in light fractions of approximately 3.4% were observed, and for vacuum bottoms, this value was approximately 6%.
- The conversion of more heavy fractions to light fractions in the thermal fixed-bed process was confirmed by the larger quantities of naphthas collected and the higher percentages recovered at temperatures close to 460°C.

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