

Research Paper

## MIDDLE DISTILLATES PIONA ANALYSIS MODIFICATION BY THERMAL CRACKING OF HEAVY MAYA CRUDE PRIMARY NAPHTHAS

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This work shows how oil fraction distillates from the heavy Maya crude batch distillation ASTM D86, are modified by their external recycling not at equilibrium but at thermal-cracking operation conditions. The observed effect of this action was mainly on raising naphtha and middle distillates yields that results from the hydrogen liberation by cracking or recombination reactions. In addition to formal experimentation, it was carried out a products characterization and PIONA analysis; and also they were compared with those obtained through Aspen Plus™ simulation. It is evident from the experimental data that mixture of light and middle distillates is enriched on paraffinic products in the range of carbon atoms numbers C<sub>5</sub>-C<sub>8</sub>, due to olefin and heavy molecules degradation.

**Keywords:** Maya crude, Primary distillation, Thermal cracking, Pyrolysis zone, Distillates yield, Hydrogen recombination

### INTRODUCTION

According to OECD world crude oil production has increased by 61% from 1971 to 2011. Growth was not constant over the period as production declined in the aftermath of two oil shocks in the early and late 1970s. Otherwise, refinery production of secondary oil products changed significantly between 1971 and 2010; the share of fuel oil in the refinery mix fell from 34% in 1971 to 14% in 2010 whereas that of middle distillates increased from 25% to 34% (OECD, 2013).

Crude oil occurs in many different forms throughout the world. An important characteristic of crude oil that affects the ease with which it can be produced is density and viscosity. In despite of its lower probed sources reserves, lighter crude oil typically can be produced more easily and at lower cost than heavier crude oil. Much of the developed nations' oil supply comes from domestic or international light or medium crude oil sources. Due to cost and availability, oil and gas companies are actively looking for processing

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heavier crude oil sources to help meet demands and to take advantage of large heavy oil reserves located in North and South America (Veil and Quinn, 2008).

However, the processing of heavier feedstocks produces some difficulties; in particular, there is a lack of precise, detailed, and systematic information as to influence, both feedstock composition and process variables on the product yields. Thermal cracking in primary distillation of oil hydrocarbons is an alternative of heavy feedstocks which are basic in petrochemical industry; right now several plants are running on kerosene, gasoil or even vacuum gas oil for producing olefins.

With the objective to improve middle distillates production, in this work was studied the effect of naphthas recycling-obtained during heavy Maya crude oil distillation-, toward the depletion zone, with the intention to favor both its thermal cracking and its sequent recombination. The indicator that was used for carry out this recombination was the PIONA (paraffin, iso-paraffin, olefin, naphthenic and aromatic compounds) analysis of each cut.

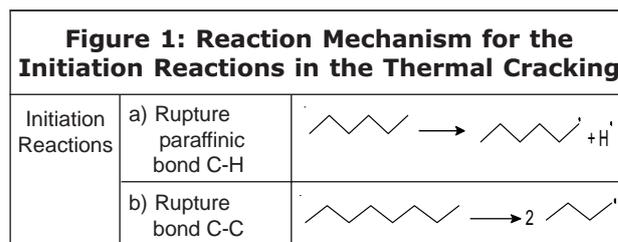
Maya crude is classified as heavy oil; the conventional distillation methods classify this crude as a mixture of paraffinic and naphthenic crude with a K factor of 11.70. Distillation of this crude have yields of: naphtha 15.3 vol %, kerosene 13.8 vol %, gas oil 34.7 vol %, and residue 61.2 vol %. To have a better idea of the quality of Maya crude it can be compared with light Isthmus-crude which have yields: naphtha 25.2 vol %, kerosene 18.3 vol %, gas oil 38.6 vol %, and residue 44.3 vol % (Manriquez *et al.*, 2000). In this comparison it can be observed the high yield of light and intermediate fractions in the light crude; on the other hand, the higher yields of the

heavy oil are mainly in the heavier fractions. Here the importance to improve intermediates cuts in the Maya crude as proposed in this work.

## THERMAL CRACKING

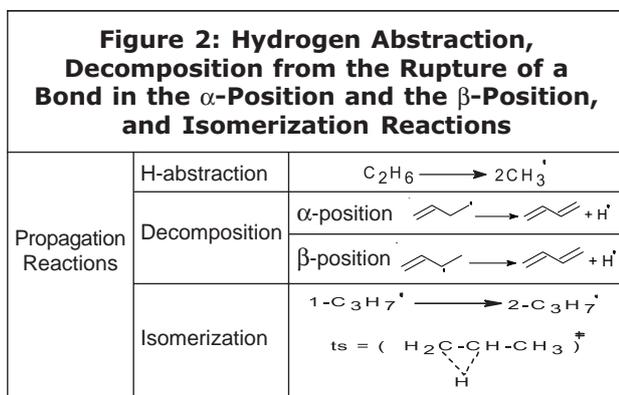
The thermal cracking reaction pathway for a hydrocarbon mixture involves free-radicals production, being these, molecules without charge, extremely reactive and with a short life. According with the hydrocarbon thermal cracking reaction mechanism, the smaller free radicals such as  $H^*$ ,  $CH_3^*$ ,  $C_2H_5^*$  are the chain carriers. Free-radical reactions involve the following steps: initiation, propagation and termination (Willems and Froment, 1988).

As is shown in Figure 1, four different types of initiation reactions have to be considered: Rupture of a paraffinic C-H or C-C bond and rupture of a bond either in the  $\alpha$  or  $\beta$ -position, with respect to a double bond. Initiation of a paraffinic bond, as well as, a bond in  $\beta$ -position proceeds through a loose transition state. The initiation of a bond in the  $\beta$ -position proceeds through a compact transition state.



As same, four several main reactions for the propagation step: Hydrogen abstraction (H-abstraction), radical addition, radical decomposition and radical isomerization are the main reactions of the thermal cracking propagation step. The parent molecule associated with the activated complex from the H-abstraction reaction is obtained by removing the hydrogen to be abstracted from the molecule and attaching the

abstraction radical to the molecule as it is shown in Figure 2.



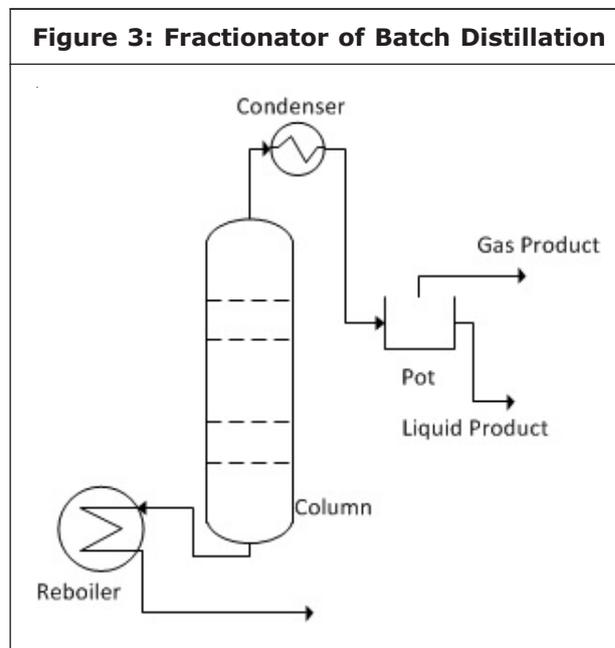
Decomposition reactions are the most important of those is the formation of a conjugated diene. Two different pathways lead to the formation of a conjugated diene: the decomposition of a radical with the free electron in the  $\alpha$ -position with respect to a double bond and the decomposition of an allylic radical. The decomposition of the 4-butenyl radical is an example of this reaction ( $\alpha$ -position), and the 3-butenyl radical is an allylic radical from which 1,3-butadiene can be formed ( $\beta$ -position). The radical isomerization in a reaction scheme for the thermal cracking of light hydrocarbons, only 1,2-isomerization reactions have to be considered. As a result, the group of radical isomerization reactions is relatively small. The structure of the activated complex is the same for every 1,2-isomerization (see Figure 2).

Finally, the termination step is the opposite process of initiation (Froment and Willems, 1988) unless the final molecule is different to the initial product of the decomposition derivate.

## EQUIPMENT AND EXPERIMENTAL PROCEDURES

Both batch (or differential) and thermal cracking distillations were carried out in a fractionator as shown in Figure 3, which is filled out with 4 mm

structured steel packed in a 0.50 m length bed. The equipment characteristics are shown in Tables 1 and 2.



**Table 1: Characteristics of Equipment Batch Distillation**

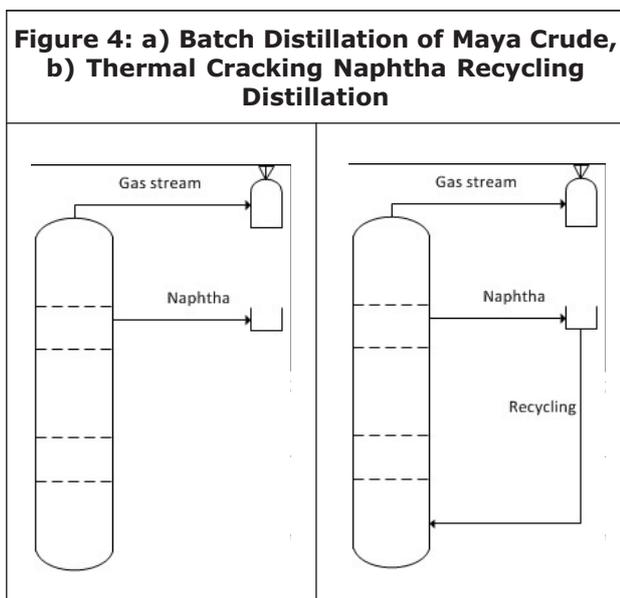
Fractionator length	1.70 m
External diameter	0.30 m
Internal diameter	0.10m
Theoretical plates number	14-18
Pack type	Structured Steel Packed Pro-Pak®
Flask container volume	1.3 L
Material construction	Stainless steel 304

**Table 2: Utility Equipment use in the Batch Distillation Tower**

Temperature Control	PID Control
Gases Trap	Trap with CO2 (Solid)
Condenser	Partial
Heating system	Electrical energy
Cooler system	Ethylene glycol
Thermocouples	3
Thermocouple type	J
Reflux pump	Peristaltic Pump
Valves	3 globe valve & 2 check valve

Table 1 shows the dimensions of the fractionators, the number of plates, volume of the flask container and the construction material. On the other hand, Table 2 shows the peripheral equipment such as gas trap, PID (proportional-integral-derivative), temperature control, thermocouples and reflux pump.

During the experimentation, the temperature was reached with a heating jacket (120 V and 400 W). The temperature range was between 300-320°C, barometric pressure was 77 kPa. The Maya crude feedstock inside the tower was 0.8 L and the recycle light fraction was constituted by naphtha. This last was feed at pyrolysis zone (see Figure 4). The differential distillation was performed according to ASTM D2892 standard (ASTM, 2013) in order to set up the operation temperature at which the naphtha can be distilled. Once this goal was reached, then, the naphtha was recycled towards the flask container to carry out the reactive distillation of Maya crude and the naphtha mixture.



The ASTM D2892 method plays an important role between the efficiency and time distillation,

providing the distillation data comparison among different laboratories. This standard method covers the procedure of distillate stabilized crude oil with a final cut temperature of 400°C, with an efficiency of 14 to 18 theoretical plates with a reflux ratio of 5:1. The theoretical plate number can be calculated with available information of the distillation tower and the data of Table 1. The operating conditions were recorded during distillation and after each cut or fraction distilled. For each cut the mass and volume record allowed us to calculate their density and distillation yield, which was calculated from the recuperated mass for every fraction with the purpose of doing a mass balance, including the liquid, gas and residue. Using temperature records we could draw a TBP (true boiling point) plot either the mass or volume. The batch distillation tower is shown in a simplified scheme of Figure 4a.

The collected naphtha was recycled towards pyrolysis zone near the reboiler, helped with a check valve and peristaltic pump. At this point higher PID temperature control was set at 300°C. This temperature is suggested by ASTM D2892 standard and reactive temperature -studied during a previous work (Guerrero, 2007)-, corresponding with the cracking temperature for the heavy oil (see Figure 4b). Over again, the operation conditions were recorded as well as mass and volume fractions.

## DISTILLATION BATCH SIMULATION

It was carried out a batch distillation simulation of Maya crude oil using the ASPEN PLUS® software, with the goal of getting an estimation of the required time to obtain distillation products working at similar conditions established in ASTM D2892 standard method procedure. The

required information to carry on this simulation was: the TBP assay, specific gravity, distillation time and reflux ratio as well as a comparison of the boiling point temperature range for each cut.

Table 3 shows the distillation intervals and physical properties for Maya crude oil, and several cuts, which belong to the simulation. The data of this Table show the ranges of TBP, ASTM D86, and ASTM D1160 for Maya crude oil,

as well as, light, middle, and heavy products respectively. These data have a minimum overlapping among the different product final boiling temperature, because of the simulation rigorous parameters. It can be observed an important relationship between the specific gravity and the increasing of the boiling temperature; being that, while the crude has less specific gravity, the final temperature of each cut will be higher.

**Table 3: Feedstock and Product Distillation Curves**

	Crude Oil		Naphtha	Kerosene	Jet Fuel	Diesel		Residue
SP @ 15°C	0.92		0.724	0.791	0.838	0.873		0.942
% Vol.	TBP	Vol. %	ASTM D86				Vol. %	ASTM D1160
0	33.31	0	36	133.05	219.41	287.91	0	221.91
5	133.29	5	63.25	146.72	233.79	301.36	5	243.53
10	178.05	10	72.57	152.3	239.63	306.78	10	252.19
30	293.35	30	103.81	164.88	250.04	316.45	30	329.85
50	404.58	50	121.49	178.04	258.68	324.6	50	443.37
70	531.97	70	135.95	193.89	268.31	333.91	70	576.69
90	711.22	90	150.44	212.6	282.35	347.92	90	853.43
95	785.40	95	161.32	224.22	292.92	358.58	95	999.85
100	877.12	100	172.19	235.85	303.49	369.24	100	1123.17

The Table 4 shows Naphtha, Kerosene and Diesel behaviors in terms of initial and final boiling point temperatures (IBT/FBT). Thus, simulation allowed us to set up the different product yields and adjust the FBT according with the configuration of the continuous primary distillation. The obtained simulation naphtha (Rizo et al., 2010)

corresponds at a lighter fraction similar with the data presented in the literature (Manriquez et al., 2000). According with the diesel product, this also was fitted and approximated with the literature data.

## EXPERIMENTAL RESULTS AND DISCUSSION

The naphtha product was submitted at a comparison of the PIONA (paraffinic, aromatic, naphthenic and aromatic) chromatographic essay between batch and thermal cracking-naphtha recycling distillations, which is shown in Table 5. From the data of this table it can be observed an important increasing of paraffin and isoparaffin

**Table 4: Comparison of the ASTM D86 Temperature Ranges Between Literature, Experimental and Simulation for the Batch and Continuous Distillation Products**

	Naphtha	Kerosene	Diesel
	IBT/FBT°C		
Aspen	36/172	133/236	288/370
Literature	36/176	177/273	274/343

**Table 5: PIONA Comparison for the Batch and Thermal Cracking-naphtha Recycling Distillations**

Hydrocarbon Families	Naphtha batch distillation		Naphtha thermal cracking-recycling	
	% Weight	%Liquid volume	% Weight	% Liquid volume
TotalP	29.76	31.75	39.51	41.29
TotalI	26.41	27.53	29.22	30.26
Total O	9.67	10.38	7.58	7.86
TotalN	19.88	18.53	17.13	15.47
TotalA	13.57	11.13	6.47	5.04
Heaviest	0.00	0.00	0.00	0.00
Not identified	0.71	0.68	0.09	0.08
Total	100	100	100	100

amount for the thermal cracking-recycling distillation (9.75 and 2.81wt% respectively). As it was expected, this variation can be attribute to the olefinic, naphthenic and aromatic compounds (minus 2.09 wt %, minus 2.75 wt %, and minus 7.10 wt % correspondingly), and not identified

compounds previously that disappeared practically (0.71 vs 0.09 wt %), which undergo the initiation, hydrogen abstraction, decomposition and hydrogenolysis thermal cracking reactions, leading at the olefins and paraffin production. During this thermal process could also be observed naphthenic compounds decreasing. The bond fragmentation is due to this behavior and therefore small molecules of paraffin and isoparaffins are formed.

Table 6 shows the detailed PIONA analysis comparison for both batch and thermal cracking-recycling naphthas by carbon number. In these data it can be observed a notable increasing of paraffinic C5-C6(37.80 versus 12.50 wt%) and isoparaffinic C6 whereas total olefin and aromatics decrease (from 23.24 wt % to 14.03 wt %). The naphthenic, saturated cyclic hydrocarbons have changed their composition from mainly C7 to C6 in both distillations.

**Table 6: Naphtha PIONA Analysis by Carbon Family for the Batch and Thermal Cracking Recycling Distillations**

Family Carbon	P		I		O		N		A	
	Batch	Cracking								
C <sub>1</sub> -C <sub>4</sub>	1.01	1.06	0.08	0.07	1.01	0.77	0	0	0	0
C <sub>5</sub>	3.34	4.22	0.97	1.16	3.18	3.03	0.47	0.99	0	0
C <sub>6</sub>	9.16	33.58	5.9	24.27	3.51	3.63	5.36	14.78	1.01	5.11
C <sub>7</sub>	12.82	0.57	10.81	3.71	1.61	0.14	10.03	1.35	4.99	0.43
C <sub>8</sub>	3.04	0.08	6.68	0.01	0.27	0	3.59	0.01	7.45	0.92
C <sub>9</sub> -C <sub>12</sub>	0.38	0	1.98	0.01	0.09	0	0.42	0	0.12	0
Total	29.75	39.51	26.42	29.23	9.67	7.57	19.87	17.13	13.57	6.46

By carbon number, it can be observed that C<sub>6</sub> PIONA compounds changed from 24.94 wt% in batch distillation to 81.37 wt% in cracking recycling naphtha distillation with an increase in saturated (p, i, n), C<sub>6</sub> compounds from 20.42 to 72.63 wt%, that it is to say also an increase in rapport saturated to non-saturated from 3.26:1 to 3:56:1, after recycling.

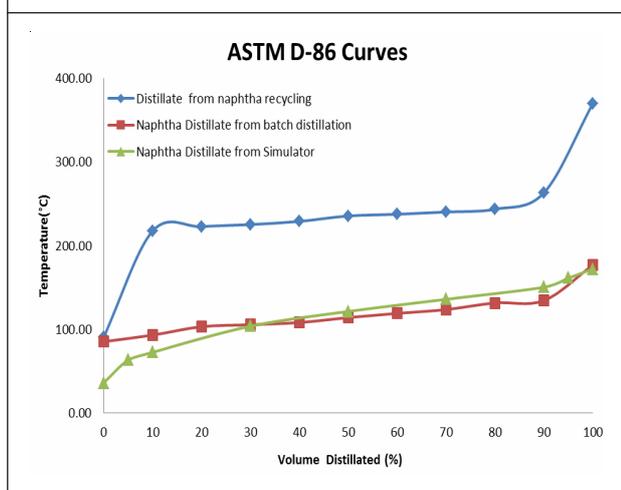
In this sense it can be attributed the formation of C<sub>6</sub> compounds at the aromatic bonds break off. On the other hand, there is another remark about the heavier carbon complexes; the C<sub>9</sub>-C<sub>12</sub> amount was declined in the thermal cracking-recycling naphtha, which it could be also attributed to the recombination of heavy compounds leading middle compounds formation.

Light fraction composition from both the batch and the thermal-cracking naphtha recycling distillations allows drawing ASTM D86 distillation curves. Figure 5 shows these ASTM D86 curves, as well as, the corresponding curve obtained from the Maya Crude Batch Distillation with ASPEN Plus®, which display a remarkable difference of 170°C in the boiling final point between the distilled fractions of the batch distillation and thermal-cracking naphtha recycling distillation. This behavior can be attributed at a higher distillation temperature provoking the heavy molecules cracking and subsequently creating low molecular weight species which are delimited between the naphtha and kerosene. A comparison between gas streams obtained from the batch and thermal-cracking naphtha recycling distillations is shown in Table 7. In the gas stream from the batch distillation; methane, butane, i-pentane and C<sub>5</sub>=/C<sub>6</sub>+ are predominant, with a lack of hydrogen and hydrogen sulfide. On the other hand, there is a notable increasing of butane; hydrogen, monoxide carbon and hydrogen sulfide formation, in the gas stream from the thermal-cracking naphtha recycling distillation.

**Table 7: Comparison of Gas Composition for the Batch and Thermal Cracking Naphtha Recycling**

Compounds	Batch Distillation (mol%)	Naphtha thermal cracking-recycling (mol%)	Difference
Hydrogen	0.00	0.47	+0.47
C5=/C6+	13.07	3.88	-9.19
Propane	0.73	8.96	+8.23
Acetylene	2.86	0.00	-2.86
Propylene	1.17	0.46	-0.71
Ethylene	0.00	0.26	+0.26
i-Butane	2.48	0.02	-2.46
Propadiene	0.00	5.35	+5.35
n-Butane	3.93	26.02	+22.09
Ethane	1.86	1.90	+0.04
1-Buteno	0.70	0.14	-0.56
i-Buthilene	0.73	0.19	-0.54
t-2-Butene	0.00	0.02	+0.02
c-2-Buteno	0.00	0.03	+0.03
i-Pentane	2.90	19.89	+16.99
Hydrogen sulfide	0.00	5.68	+5.68
n-Pentane	0.00	24.92	+24.92
Methane	69.57	0.76	-68.81
Carbon Monoxide	0.00	1.04	+1.04

**Figure 5: ASTM D86 Curves for the Liquid Products Batch and Thermal Cracking Naphtha Recycling and Aspen Plus Distillations**



An important remark in Table 8 is related with the composition of these gas streams, which corresponds with an initial sampling and not an average composition during the batch and thermal cracking naphtha recycling. It can be assumed that the H<sub>2</sub>S, H<sub>2</sub> and CO will increase during the distillations as a result of the thermal desulfurization, cracking reactions mainly hydrogen abstraction and hydrogen transfer, which produce hydrogen radicals.

## CONCLUSION

This work has the intent to know how the middle distillates can be modified by the naphtha recycling in the Maya crude batch distillation working at thermal-cracking operation conditions.

The first results have shown that is possible to enhancing naphtha yield at similar levels found with light crude oils distillation by the naphtha recycling into the thermal cracking zone in the distillation column. This improving is a result of the cracking reactions such as hydrogen abstraction and hydrogen transfer, as well as, the thermal desulfurization, which produce olefins, paraffins, iso-paraffins and small amounts of hydrogen. This production is reflected in the naphtha composition and the boiling point temperature. The primary naphtha recycled allowed to change the naphtha carbon range from C4-C12 to C5-C8, which is also reflected as an increasing of the ASTM D86 temperature distillation curve. Nevertheless, this behavior in a constant temperature zone was identified in the % volume range between 20-80%, where the concentration of olefins and paraffins is higher compared with the total distillation range. The gas stream also suffers a modification in its composition, hydrogen and hydrogen sulfide has been produced also by the cracking reactions. The results shown are specific for the 100% level of recycled primary naphtha in the direction of the change: from unsaturated (olefins, aromatics and naphthenic) to saturated molecules (paraffins and iso-paraffins); therefore, in the case of requiring an intermediate composition, its feasibility would be allowable by partial recycling.

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