



# International Journal of Engineering Research and Science & Technology

ISSN : 2319-5991  
Vol. 4, No. 4  
November 2015



[www.ijerst.com](http://www.ijerst.com)

Email: [editorijerst@gmail.com](mailto:editorijerst@gmail.com) or [editor@ijerst.com](mailto:editor@ijerst.com)

Research Paper

# MAYA CRUDE OIL PRIMARY NAPHTHA THERMAL CRACKING REPRESENTATION BY MODEL COMPOUNDS FROM PIONA ANALYSIS

Pavel Rizo-Acosta<sup>1\*</sup>, Guillermo Villagran-Gutierrez<sup>2</sup>, Jose A Davila-Gomez<sup>2\*</sup>,  
M Teresa Linares-Vallejo<sup>3</sup> and Jose A Muñoz-Arroyo<sup>3</sup>

\*Corresponding Author: Pavel Rizo-Acosta and Jose A Davila-Gomez  
✉ [pavel601@gmail.com](mailto:pavel601@gmail.com) and [jadg@azc.uam.mx](mailto:jadg@azc.uam.mx)

From the PIONA analysis of Maya crude primary distillates it was emulated a representative hydrocarbon model compounds mixture with n-heptane, isooctane, cyclohexane and xylene; was not employed olefin at all. Model compounds were obtained from lab reagents purified by Separar espacio. sS se repite, solamente en amarillo mas adelante. ASTM-D86, DD differential distillation. The emulated primary oil naphtha cut was introduced to a null metallic oxides gasoil residual, obtained by distillation from more than 250 °C, and induced to thermal cracking over 180 °C and recycled distillate, RD to reboiler. Comparison between both DD and RD distillations were carried by means of normal ASTM-D86 method which show pertinence of emulating multicomponent primary oil naphtha by four model compounds. RD gas and liquid products show good presence of hydrogen and olefins providing one by side method of both for in situ hydrogen recombination and olefin production. This work suggests performing studies with metallic oxides as catalysts as well as sulfured compounds in a model compounds mixture with the objective to study new systems that allow to widely understanding the pyrolytic thermal effect during crude primary distillation and in this way to optimize heavy Maya crude oil distillation gasoline yields.

Keywords: Maya crude, Model compound mixture, PIONA primary distillation, Thermal cracking, Pyrolysis zone, Hydrogen recombination

## INTRODUCTION

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 spite of its slower probed sources reserves, lighter crude oil typically can be exploited more easily. Much of the developed nations' oil supply comes from

<sup>1</sup> UPEST-CNRS Chimie, Thiais, Fr.

<sup>2</sup> UAM-Azcapotzalco, EnergyDept.Mexico, Mx.

<sup>3</sup> IMP. MexicoCy, Mx.

domestic or international light or medium crude oil sources (Veiland Quinn, 2008). Whereas, the oil producers have stocks are forced to use heavier feed stocks in their own refinery process, which is the case of crude exporter's countries like ours.

The conversion of heavy petroleum fractions into valuable products has been one of the objectives for upgrading heavy petroleum oils. At present this conversion is mainly achieved by thermal cracking and/or catalytic hydrocracking. A lot of studies are run on catalytic processes, for that reason this work focuses on thermal reactive cracking, the other major of the hydrocarbon chemical industry.

In heavy oils, hydrocarbon thermal cracking process of higher molecular weight compounds can be transformed to lighter hydrocarbon products by pyrolysis processes at a higher temperature. For being economical, the development of thermal cracking processes must be accompanied by large amounts of gas and naphtha output.

Thermal cracking of hydrocarbons involves many radical steps and leads to a wide spectrum of products. Radical reactions involved in thermal cracking can be classified in three broad categories: initiation, propagation (consisting of hydrogen-abstraction and radical decomposition), and termination; Interwoven with these reactions is radicals isomerization (Froment, 1981).

Cracking is a phenomenon by which higher boiling constituents in petroleum are converted into lower boiling hydrogenated products. Materials that have boiling range higher than gasoline and kerosene may (depending upon the refining options) be referred to as recycling stock, that is say, to be recycled into the temperature

cracking zone equipment until conversion is accomplished. Recycling to the thermo dynamically equilibrium plate is not preferable solution as showed by Davila *et al.* (2008).

Metallic constituents are found in every crude oil as oxides and organometallic molecules. Metals affect many upgrading processes and cause particular problems mainly by poison sulfur and nitrogen removal catalysts as well as other catalytic processes.

Two groups of elements appear in significant concentrations in the original crude oil associated with well-defined types of compounds: a) zinc, titanium, calcium and magnesium appear in the form of organometallic soaps with surface-active properties adsorbed in the water or oil interfaces which act as emulsion stabilizers; b) vanadium, copper, nickel and part of the iron found in the crude oils seem to be a different class and are present as oil-soluble compounds (Speight, 2006).

Maya crude whom primary naphthas were worked in former research, has metallic oxides from b) type and then, manifested great activity on pyrolysis and hydrogen recombination by recycling the first condensates to a 150 °C moderate temperature (Rizo *et al.*, 2014).

Model compounds selection was taken in base of the work carried out above mentioned by Rizo *et al.*; these researchers made a Maya crude and naphtha reactive distillation experiment and there characterization of the first distillates. This characterization gave mainly the paraffinic, iso-paraffinic, olefin, naphthenic and aromatics (PIONA analysis) as percentage of each contained in this cut. The results are depicted in Table 1.

From data of this table it can be observed two higher values in both weight % and volume %

Table 1: Middle-Distillate PIONA Characterization of the Maya Crude as a Reference to Modelling by Pure Compounds Selection (Rizo et al., 2014)			
Hydrocarbons Family		Weight %	Volume %
Total	P	29.76	31.75
Total	I	26.41	27.53
Total	O	9.67	10.38
Total	N	19.88	18.53
Total	A	13.57	11.13
Non identified		0.71	0.68
Total		100	100

corresponding to paraffin and iso-paraffins; afterwards, two more medium values corresponding to naphthenic and aromatic compounds and, finally, the lowest value of all, which represents the olefins presented in this middle distillate.

Taking in account the above information we have proceeded at the selection of model compounds more representative of that mixture while checking the lab reagents stock. The compound most representative for paraffins was n-heptane, for iso-paraffins was iso-octane, cyclohexane for naphthenic and xylene for aromatic compounds respectively. It is important to mention that, the olefin compound was not selected because not lab availability and should be synthesized and purified in situ, which may be the next goal.

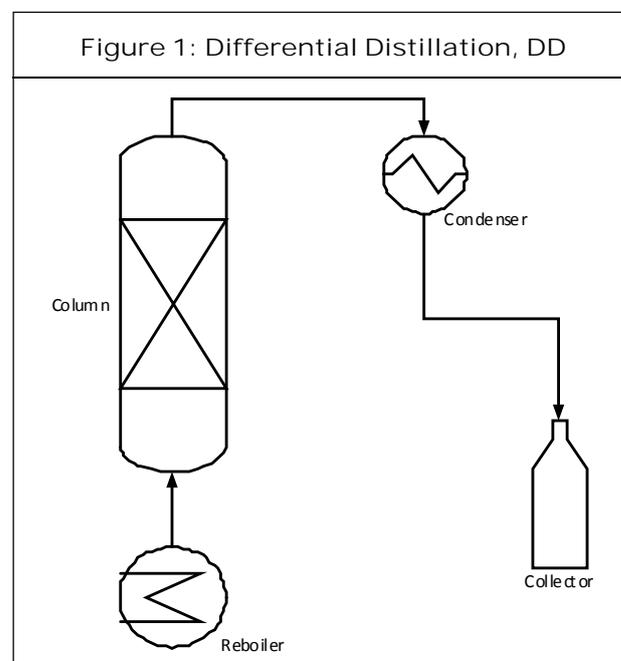
Thus, then, the final volume percentage taken of each one was: n-heptane 30%, isooctane 30%, cyclohexane 20% and xylene 20%. Due to the complexity of crude oil because of great amount of compounds, these four model compounds are extremely helpful in order to know the main reactions, which are involved during thermal

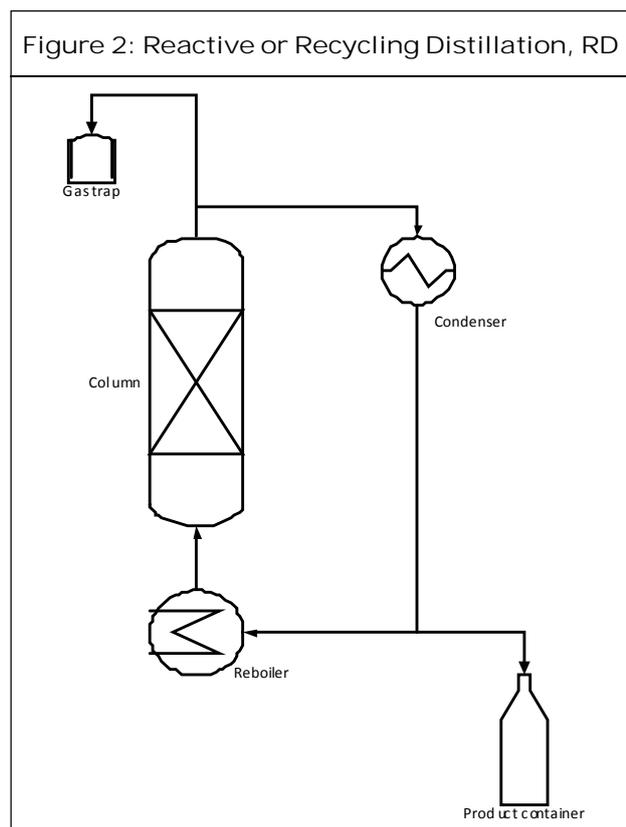
cracking as well as, to have a suitable knowledge about the pathway of these cracking reactions.

## EQUIPMENT AND EXPERIMENTAL PROCEDURES

It was carried out two sort of distillations; first, Differential Distillation (DD); second, reactive or Recycling Distillation (RD). As can be observed in Figures 1 and 2, these distillations were performed at a lab level varying mainly the recycling in one of them. During DD the temperature range was operating from 84 °C to 180 °C (Guerrero *et al.*, 2009); the model compounds mixture volume was 100 mL, which was constituted by n-heptane, iso-octane, cyclohexane and xylene, this emulating a PIONA mixture, was renamed PIONA (Ø, because non olefin added). With the objective to get its ASTM curve according to the standard method ASTM-D86.

In Figure 1, is shown the model compounds DD as a standard ASTM-D86 distillation. The





system was assembled by reboiler, rectification column, condenser and product collector.

When RD was performed the range temperature used was from 170 to 180 °C, the same model compounds mixture (100 mL) and some higher distillate diesel compounds (150 mL) were got together. Then, the product collected was recycled to the pyrolysis zone and re-distilled; finally, it was collected liquid and gas products.

Figure 2 displays the reactive distillation equipment. As a difference of the DD, this system also has a gas trap as well as a recycling product container.

## RESULTS AND DISCUSSION

### Model Compound Selection and Oil Naphtha Fitness

Four molecules were selected as model

compounds for mixturing (MC): n-heptane for paraffins, isooctane for isoparaffins, cyclohexane for naphthenic and xylene for aromatics in proportions mentioned above; as individuals, it was performed for each an normal ASTM-D86 curve in order to assure their quality as pure substance, like it can be seen in Figures 3 a, b, c and d. Probes for MC mixturing were taken from +50% distillates.

In Figure 3, a) it is embossed the normal ASTM curve for n-heptane reaching a maximum temperature of 97 °C, b) it corresponds to isooctane with 99 °C, c) cyclohexane at 79 °C and d) xylene with a maximum point of 138 °C. It can be easily identified how the lower temperature is for naphthenic compound and the higher for aromatic model compound.

The portion of each reactive compound taken for mixture PIØNA to emulate crude oil Maya primary distillates for recycling thermal experiments was selected from the +50% volume DD individual distillates; then, mixture PIØNA was obtained by molecules distilling in the final isothermal individual range.

Figure 4 shows comparison of ASTM curves performance between crude oil naphtha and model compound mixture crude emulate: 10 °C mean temperature difference can be observed between initial and final distillation. Comparing both, oil naphtha and MC mixture ASTM DD curves, MC mixture fits well oil naphtha as cited.

### DD and RD for MC Mixture

After formulation the MC mixture by integrating individual model compounds, there were performed characterization curves, both DD and RD, as it can be seen in Figure 5. Observed difference between DD and RD is due to thermal decomposition for MC mixture.

Figure 3: ASTM-D86 DD Curves for Each Model Compound

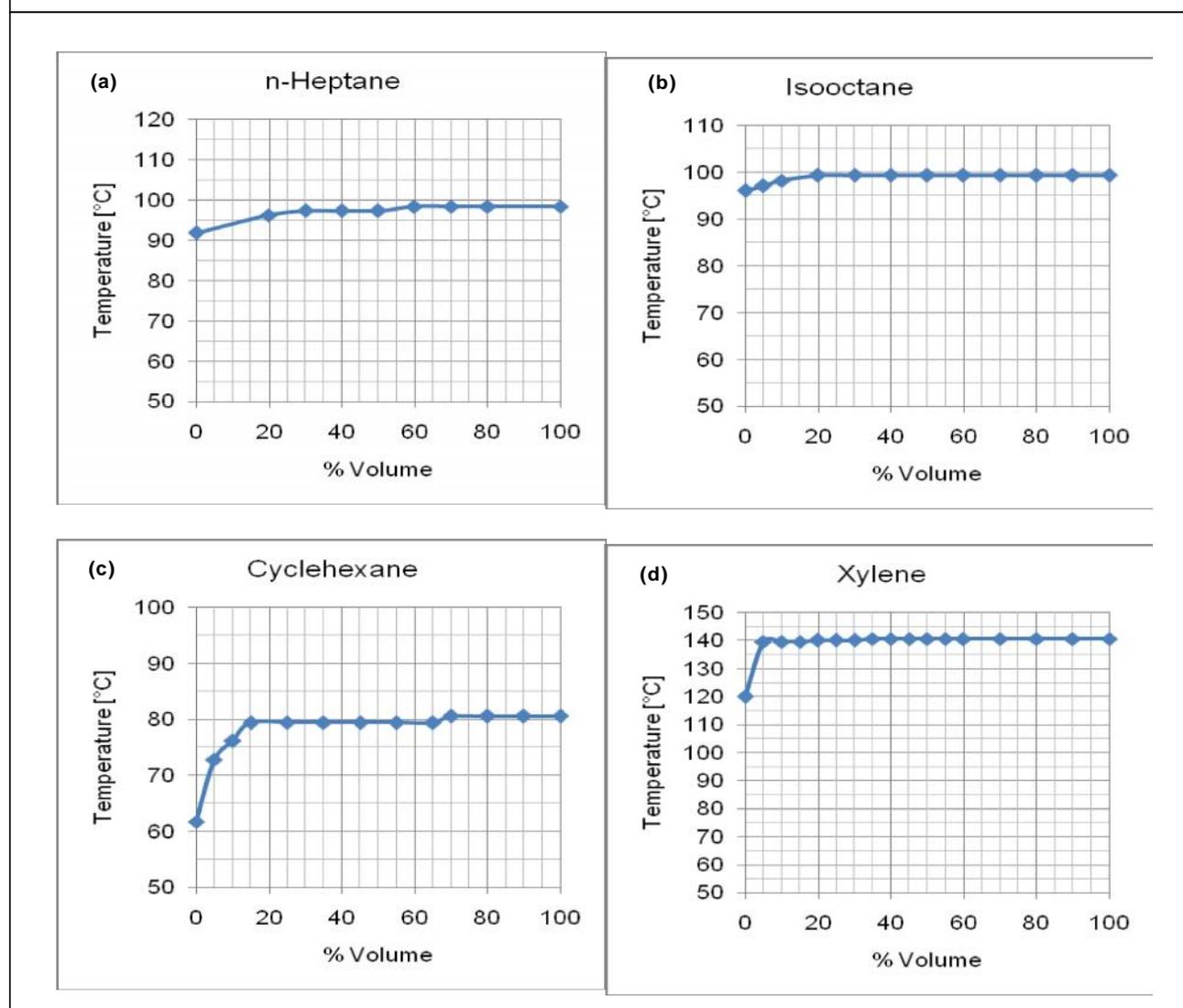


Figure 4: Maya Crude Distillate and Model Compound ASTM Curves

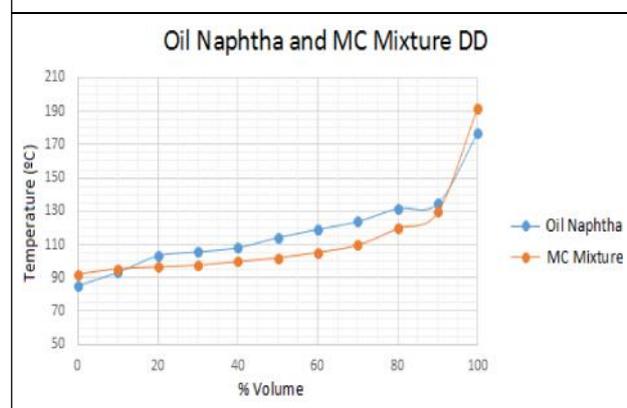
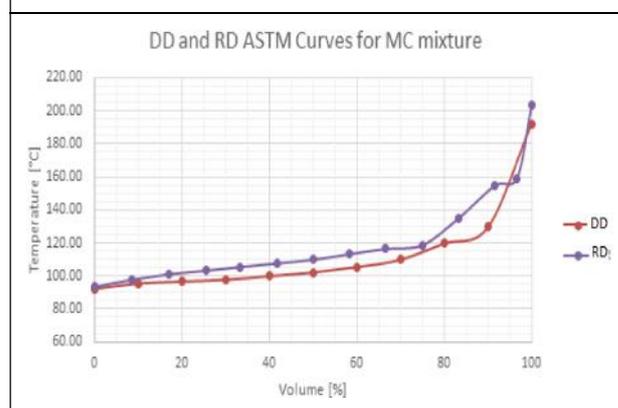


Figure 5: (a) ASTM Curves for DD Model Compound Mixture and (b) RD Distillation



Both, ASTM-D86 assays, start at same temperature of around 90 °C, increasing gradually at several slopes as far as % of distilled volume, from this 20 % to 70% there is a constant change and from 70% to 100% it is shown a significant variation. The fact of RD curve shows temperatures higher than DD curve for volume distillates means that at least one compound has entered decomposition. In fact, gas and liquid, condensates and remnants products had been chemically analyzed by means of gas and liquid chromatography using different in lab available techniques.

For gas product, after vapors condensing drying, characterization was carried out by gas chromatography method of "refinery gases". carried out at the Mexican Institute of Petroleum; which results presented in Table 2.

	Time (min)	%
Hydrogen	2,056	71,87
C5=/C6+	2,956	23,64
Propane	5,415	0,25
Propylene	5,982	0,28
Ethylene	6,199	3,42
1-Butane	7,783	0,01
t-2-Butene	9,226	0,06
Carbonmonoxide	17,726	0,17
Methane	18,629	0,29

This table depicts the gas products of the reactive distillation, where is observed the main product is hydrogen (approximately 72%), olefins C5=/C6+ and ethylene (in almost 27%), in a good measure in comparison with the others compounds. It is also observed that these gas products are different to the model compounds

of the feedstock. Furthermore, model compound mixture had non olefins nor metallic oxides of any kind, so this observed cracking only can be from thermal degradation origin, thus providing evidence of different mechanism from oil crude naphtha cracking, in fact Maya oil crude contents until 70,000 ppm of metallic oxides as has been reported previously.

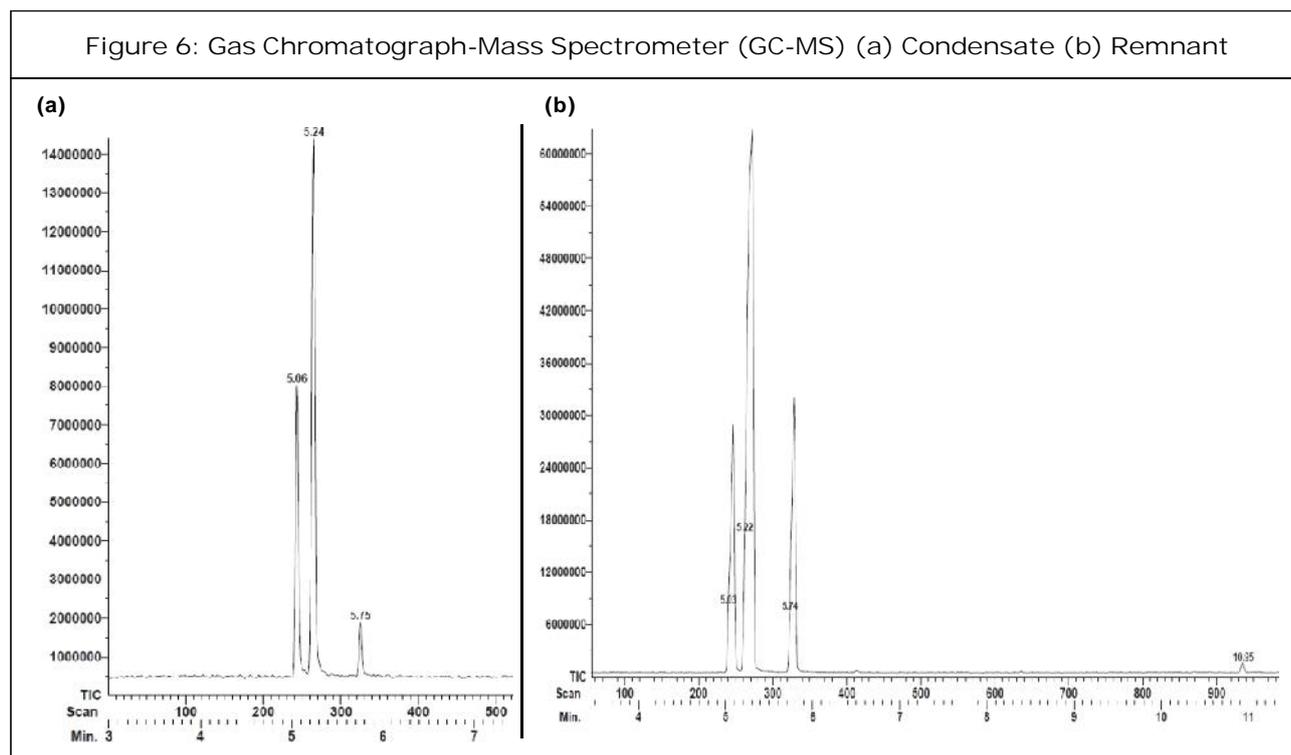
For liquid, it was performed a liquid chromatogram LC, of both RD condensate product and mixture remnant, whose results are shown in Table 3.

Composition	B. P. (°C)	Condensate	Remnant
		%w	
C5 to C12	41 a 220	78,2	77,4
C13 to C14	221 a 254	21,8	22,6

In this Table it is presented two cuts at different boiling point temperature and carbon composition, as well as the present weight percent of both condensate and remnant liquid products; at first seen it tells us that there are little (if any), difference between them.

Depending on the calculation method for the interpretation of the previous values, condensate contain between 1% and 5% over of light compounds C5 to C12 than in the remnant, which confirms both low thermal disintegration obtained and the quality of the experimental method to support hydrocarbon null of metallic oxides as used in former work. A later on work using specific metallic oxides to evaluate their catalytic action in composition and degradation can be assumed to be done.

Similarly, this table shows that both liquid condensate and remaining kept little difference between them, suggesting more a result of the thermodynamic equilibrium between the fractions



(lighter in the condensed distillate than in the remaining), however, since in the production of gas from the thermal cracking there are about a quarter of olefins in vapor form also, it is expected that in the condensed, and probably in the remaining liquid indeed, there are C5=/C6+ olefins in its liquid form.

As an additional chromatogram essay it was performed a Gas Chromatograph-Mass Spectrometer (GC-MS), Figure 6 shows both studies: condensate and remnant.

In Figure 6, it can be seen that compounds obtained in the residue have correspondence with compounds of model mixture employees even if degraded by reactive distillation: isoparaffins, paraffins, naphthenic and aromatics and, surely, secondary olefins incorporated and in balance with the corresponding ones in the gases produced as distillation went by. Thus, comparison of peaks values for two chromatograms are given in Table 4, below:

Table 4: Condensate and Remnant Compounds Comparison

Peak	Time (min)	Condensate (% Area)	Remnant (% Area)	Diference Cond - Rem
1	5.03 - 5.06	30.8	18.65	12.15
2	5.22 - 5.24	62.99	61.37	1.63
3	5.74 - 5.75	6.21	19.43	-13.22
4	10.95	0	0.55	-0.55

Notes, in the table above, that distillation remnant residue peaks show, regarding to condensate's, significant changes: indeed, the compounds associated with the first peak increase from 18.65 to 30.80%, response area; those of second peak from 61.37 to 62.99, while following two peaks decrease: third one from 19.43 to 6.21 and fourth just disappear.

Result changes of the recirculation of primary distillates to pyrolysis zone (thermal degradation), in behavior similar to that obtained in previous studies: while the naphthenic and aromatic disappear (or diminish) their presence; paraffins

are strengthened, i.e., there is net paraffinization of distillate obtained by this way (93.79% in recirculated distillate against 80.02% in remaining).

## CONCLUSION

The four model compound mixture prepared from PIONA analysis of Maya crude primary cut, follow an ASTM-D-86 curve behavior quite similar to that of multicomponent naphtha Maya crude which can be interpreted as an excellent representation for this cut.

Here, partial conclusions enlisted

- From the PIONA analysis of Maya crude primary distillates it was emulate a representative hydrocarbon model compounds mixture.
- Model compounds suitable for particular mixture were n-heptane, isooctane, cyclohexane and xylene; it was not employed olefin at all.
- Model compounds were obtained from lab reagents and re-purified by ASTM-D86 distillation.
- The emulated Maya crude primary cut was introduced to a non-metallic oxides gasoil residual distilling from more than 250 °C for recycling distillates.
- Chemical analysis of gases from recycling RD shows big presence of hydrogen and olefins (and paraffin trace, also), which strengthens the hypothesis that observed degradation in previous research was driven by catalytic action of present metals and reinforces the idea of insuring, in oil primary distillation, hydrogen recombination by recycling part of such distillates to its pyrolysis zone (instead of to the equilibrium plate).

- Observed the production of olefins in the cracked gases indicates a good thermal degradation of heavy molecules, aromatics and naphthenic: xylene and cyclohexane; the large amount of hydrogen is proved clear of the initiation, propagation and termination processes of recombination.
- Distillate and remnant liquid chromatographic analysis show, revalorization of the RD condensate paraffins content while aromatics and naphthenic thermal degradation are confirmed.

This work suggests the need to perform studies with metallic oxides as catalysts as well as sulfured compounds in a model compounds mixture, with the intention of analyze the pyrolytic effect, catalytic cracking, and/or desulfurization, with the objective to study new systems that allow to widely understand the pyrolytic effect during crude primary distillation and in this way to optimize heavy Maya crude oil distillation yield to gasoline.

## REFERENCES

1. Davila J A, Delgado L and Castellanos M (2008), "Hydrogen Strategy on Petrol Processing", 19 International U. O. Chemistry Conference, Stgo., Cuba.
2. Froment G F (1981), "Thermal Cracking for Olefins Production", *Fundamentals and their Application to Industrial Problems, Chemical Engineering Science*, Vol. 36, No. 8, pp. 1271-1282.
3. Guerrero A, Davila J A and Delgado L (2009), "Pirólisis e Hidrogenación in Situ de Crudos Pesados con Naftas", *Tecnología Química*, Vol. 29 (Edición Especial), pp. 143-152.

4. Rizo P, Davila J A, Delgado L, Linares M T and Muñoz J A (2014), "Middle Distillates PIONA Analysis Modification by Thermal Cracking of Heavy Maya Crude Primary Naphthas", *Int. J. Engg. Res. & Sci. & Tech.*, Vol. 3, No. 3, pp. 172-178.
5. Speight J G (2006), *The Chemistry and Technology of Petroleum*, 4<sup>th</sup> Edition, CRC Press, ISBN: 0-8493-9067-2.
6. Van Camp C E, Van Damme P S and Froment G F (1984), "Thermal Cracking of Kerosene", *Industrial & Engineering Chemistry Process Design and Development*, Vol. 23, No. 1, pp. 155-162.
7. Veil J A and Quinn J J (2008), "Water Issues Associated with Heavy Oil Production", Environmental Science Division, Chicago University.



**International Journal of Engineering Research and Science & Technology**

**Hyderabad, INDIA. Ph: +91-09441351700, 09059645577**

**E-mail: [editorijerst@gmail.com](mailto:editorijerst@gmail.com) or [editor@ijerst.com](mailto:editor@ijerst.com)**

**Website: [www.ijerst.com](http://www.ijerst.com)**

