THE EFFECT OF COMPOSITION OF CONDENSED FRACTIONS' MIXTURES OF A VENEZUELAN RESIDUE ON THE DELAYED COKING PRODUCTS QUALITY

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***Abstract*— The effect of the composition of resin and asphaltene on the quality of delayed coking products was evaluated. 10 mixtures with a controlled composition of S.A.R.A. (Saturates, Aromatic, Resin, Asphaltene) fractions with high percentage of resin and asphaltene, obtained from a vacuum residue of Venezuelan crude commercially known as "Merey", were processed in a laboratory scale delayed coking unit. The physic-chemical characteristics of the mixtures and products (distilled and coke) were obtained. Results indicate that on increasing the resin and asphaltene content, there is a decrease in volatile material content and an fixed carbon and ash increase. Metal and sulphur content was lower in coke from resin' rich mixtures while it was higher in asphaltene' rich mixtures. This showed the impact that the S.A.R.A composition of the feed has on the products quality.**

***Keywords*— Delayed coking, S.A.R.A, Yield, Condensable liquids, Coke.**

I. INTRODUCTION

Delayed coking is the most commonly used thermal treatment for heavy and extra heavy crude in Venezuela as a process for deep conversion of crude which permits obtaining higher commercial value products. This process is fed mainly by the short residue coming from the vacuum distillation which is thermally treated and where two types of endothermic reactions take place: one involving cracking to obtain liquid and gas products and the other, polymerization-condensation in which coke as a solid product, is obtained (Nava, 2017).

Previous works (Meza-Avila *et al*., 2016; Meza *et al*., 2018), showed the need to study the separately impact of the S.A.R.A fractions of the crude oil. on the yield and characteristics of the delayed coking products in general, and specifically in the case of Venezuela, as a narrow range of feed composition had been studied in the past (Linares, 2003; Requena *et al*., 2008; Salazar *et al*., 2015; Bello *et al*., 2006), that it is necessary to extend (Meza *et al*., 2018) .

The detailed effect of these fractions in Venezuelan crude was shown in Meza-Avila *et al.* (2016) and Meza *et al.* (2018), indicating that more in-depth research on the fractions influence was needed to determine and show the possible synergy existing between the crude fractions through a feed composition controlling process, with a specific amount of each fraction within the mix fed to the reactor. The effect of the presence of aromatics has already been established (Nava *et al*., 2017) and so the remaining fractions, resins and asphaltenes, which are found in greater proportion in Venezuelan crude, are now evaluated.

As a result, this research presents the evaluation of the effect of resin and asphaltene on the delayed cooking products quality (condensable liquids and coke).

Ten mixtures with S.A.R.A fractions controlled composition were processed; five resin rich and five asphaltene rich. These fractions were obtained from a 16° API vacuum residue of Merey heavy crude from the east of Venezuela. Coking was done in a laboratory scale delayed coking unit located in the Carbon and Petroleum Residue Laboratory at Simon Bolivar University, and the physic-chemical characteristics of the mixtures and condensable liquid products and coke were obtained.

The aim of this research is to propose improvements to the delayed coking process, with the use of a local sample, by evaluating the behavior of Venezuelan typical residues through a more exhaustive study which, unlike previous work, is an evaluation of the profile of the fractions content. This would allow the identification of tendencies that exist between the products quality and the resin and asphaltene composition in the feed.

II. METHODS

A. Feed preparation for the delayed coking process

The preparation of the feed (mixtures) for the delayed coking process was done by varying the weight percentages of each one of the S.A.R.A. fractions. The fractions were obtained using the methodology put forward by Zerpa (2016) insuring that the absorbents were used immediately on completion of their activation process. Ten mixtures were prepared for the delayed coking process; five with high resin content and five with high asphaltene content following the composition seen in Table 1 (Nava, 2017) (σ= standard deviation).

B. Laboratory scale delayed coking process

The delayed coking was done in a laboratory scale unit used by Salazar *et al.* (2015), Meza-Avila *et al.* (2016) and Meza *et al*. (2018), with the size reactor modified to

0,7 x 12 cm, being smaller than the one used in this previous studies. The established operational conditions of the new reactor and the new load (2 to 2,5 g) were: temperature 650 ºC, reaction time 60 min, heating ramp 5 ºC/min and 150 ml/min of nitrogen as the carrier gas. These operational conditions remained constant for the thermal treatment for each one of the mixtures and the operation of the delayed coking unit was carried out following the steps outlined by Da Fonseca and Ruiz (2014).

C. Characterization of delayed coking feed and products

The physic-chemical characteristics of the Merey vacuum residue, the mixtures prepared as feed for the delayed coking process and their products: condensable liquids (distilled) and solids (coke, were obtained using the tests listed next:

- Thermogravimetry: ASTM E1641.
- Proximate analysis: ASTM D5142.
- Elemental analysis: COVENIN 2596-89 (for C), ASTM D4239-05 (for S).
- Metals: EPA-6010.
- Simulated distillation: ASTM D2887-16.

III. RESULTS

Using Zerpa's methodology (Zerpa, 2016), a S.A.R.A. separation of the Merey vacuum residue was carried out on a larger scale, to obtain the hydrocarbon fractions with which the mixtures for the feed in the delayed coking process were prepared, following the compositions shown in Table 1 in the Methodology section.

Once the 10 mixtures were prepared with the representative amounts of resins and asphaltenes, they were subjected to the delayed coking process on a laboratory scale. The yields for coke, distillates and non condensable products were determined.

The yields obtained for the resin rich mixtures ranged between 28 to 41 %w for coke, 24 to 41 %w for distillates and 48 to 18 %w for non condensable, when the composition of said fraction of hydrocarbons was increased. On the other hand, the yields for asphaltene rich mixtures ranged between 43 to 68 %w for coke, 0.4 to 0.8 %w for distillates and 57 to 31 %w for non condensable with an increase in the asphaltene composition of the feed to the delayed coking process (Nava, 2017).

A proximate analysis shown in Fig. 1 was done from the curves obtained through thermogravimetry analysis of the Merey vacuum residue and the mixtures.

This analysis of the Merey vacuum residue and the ten prepared mixtures shows a low moisture content of less than 0.1 %w, a volatile material which ranged between 84.41 to 48.55 %w and values for the sum of fixed carbon plus ash between 15.58 to 51.45 %w.

Figure 1 shows that the volatile material was greater in the Merey vacuum residue followed by the 5 resin rich mixtures and then the 5 asphaltene rich ones. The volatile material diminished for the 5 resin rich mixtures with the increase in the composition of said fraction and the same tendency was seen with the increase in the composition of the asphaltene fraction.

This trend could be linked to the fact that the maximum conversion of cracking occurs in this order: saturates>aromatics>resins>asphaltenes, as the conversion of each one of these hydrocarbons decreases with the increase of the aromaticity and molecular weight of each fraction (Guo *et al*., 2008), highlighting that the Merey vacuum residue has a lower resin and asphaltene content compared to the prepared mixtures. Therefore, a mixture with a greater content of the more condensable fractions will have a lesser conversion of cracking and thus a lower presence of volatile material.

In the case of the content of fixed carbon plus the ash, inverse behavior was found. This content was lower in the Merey vacuum residue and then grew with the increase in the resin content and finally, higher results were obtained with an increase in the asphaltene content of the prepared mixtures. The tendency indicates a greater yield in coke in the same measure as the resin and asphaltene content of the mixtures increases.

These findings were expected as it has been shown that coke formation is determined by the aromaticity and molecular weight of the fractions involved (Guo *et al*., 2008); therefore, the results obtained confirm that on having a lower asphaltene content in the feed to the delayed coking process, the formation of coke is inhibited and it contributes to the formation of volatile material.

A lower yield in coke is expected for residues that have a greater composition of saturates and aromatics while a higher yield in coke is expected for residues which have a larger content of resins and asphaltenes.

Table 1. Mixtures prepared for the delayed coking process.

Sample	Fraction (%w) ± σ			
	Aromatics	Saturates	Resins	Asphaltenes
50% Res	8 ± 1	21 ± 1	50 ± 1	21,0 ± 0,1
60% Res	7 ± 1	17 ± 1	60 ± 1	17,0 ± 0,1
76% Res	5 ± 1	9 ± 1	76 ± 3	9,0 ± 0,1
90% Res	2 ±1	4 ± 1	90 ± 1	4,0 ± 0,1
96% Res	2 ± 1	2 ± 1	96 ± 1	0,0 ± 0,1
50% Asp	8 ± 1	21 ± 2	21 ± 3	50,0 ± 0,1
60% Asp	6 ±1	17 ± 2	21 ± 3	60,0 ± 0,1
75% Asp	4 ± 1	11 ± 2	11 ± 3	75,0 ± 0,1
90% Asp	2 ± 1	4 ± 2	4 ± 3	90,0 ± 0,1
100% Asp	0 ± 0	0 ± 0	0 ± 0	100,0 ± 0,1

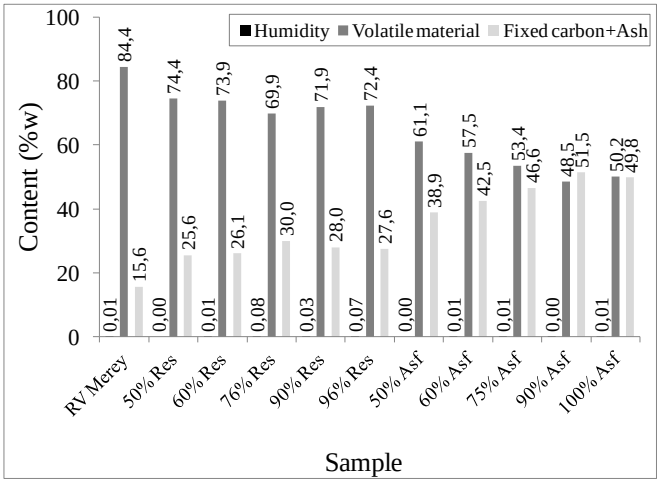

Figure 1. Proximate analysis of the Merey vacuum residue and the prepared mixtures

A thermogravimetry analysis of the coke obtained from the delayed coking process was also carried out (Nava, 2017), from which the results of the proximate analysis were obtained (Fig. 2). The coke obtained from the resin and asphaltene rich' mixtures was studied using this analysis, especially those corresponding to the coking of the mixtures with 60, 90 and 96 %w resin and 50 and 75 %w asphaltene.

The coke sample analyzed showed negligible moisture content, below 0.3 %w; volatile material was less in the coke from the resin rich mixtures (between approximately 10 and 12.30 %w) and greater for the coke from the asphaltene rich mixtures, up to 29.15 %w corresponding to C50% Asf. As a result, there was a higher content of fixed carbon and ash in the coke from the resin rich mixtures with minor differences which are not representative of the increase in the resin content in the feed, as a coke with an equivalent thermal stability was obtained.

Coke from the asphaltene rich mixtures showed a greater variation in the results for the volatile material, fixed carbon and ash as a greater amount of volatile material was trapped within, which could be due to that the reaction time is not being sufficient for a larger amount of volatiles to be released in the delayed coking process (Nava, 2017).

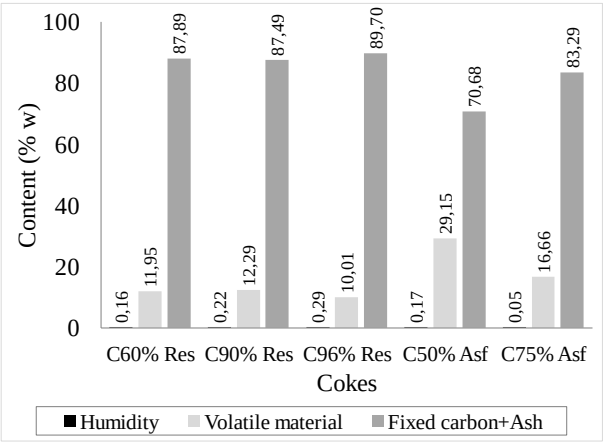

Figure 2. Proximate analysis of the coke obtained

This result could also be linked to the type of coke formed structure, as it has been found that the type of the optical texture formed is directly proportional to the feed aromaticity in the delayed coking process (Eser and Jenkins, 1989). Poor resin and asphaltene feeds give rise to sponge coke in the process while rich resin and asphaltene ones create an isotropic structure with low porosity (Rhedey and Du Themblay, 1977). It is therefore likely that during its formation, the more porous structures (with greater resin content) allow the release of the volatiles formed in the process with greater ease, thus resulting in a poor volatile coke, while the less porous structures (asphaltene rich) generate a coke that would be a type of trap for the volatile compounds, hindering their release once they are formed and creating a coke with a higher volatile substance content than in the other cases.

The carbon and sulphur content was measured to determine the S/C ratio present in the Merey vacuum residue, the prepared mixtures and the coke obtained. Fig. 4 shows the findings for the residue, two resin rich mixtures (60 and 90 %w), two asphaltene rich (50 and 75%w) and the coke obtained in each case from delayed coking.

Figure 3.a shows a similar result to the carbon content in the vacuum residue and the mixtures. From these findings, no conclusion on an existing tendency between the carbon content and the resin and asphaltene composition in the mixtures for the feed in the delayed coking process and the corresponding coke could be reached. In these cases, the calculation of the C/H and S/C atomic relation is more useful for making a preliminary analysis of the samples analyzed condensation degree (Requena, 2007). The sulphur content (Fig. 3.b), reveals a lower proportion of this compound in the Merey vacuum residue and higher proportions for the resin and asphaltene rich mixtures. This is due to, the resin and asphaltene fractions having a greater number of heteroatoms in which sulphur plays a more important role. On comparing the results of the resin rich mixtures with those of asphaltene rich ones and the respective coke obtained from the delayed coking process, it was found that there was a slightly higher result for the asphaltenes but with lower differences, that did not exceed 1%w.

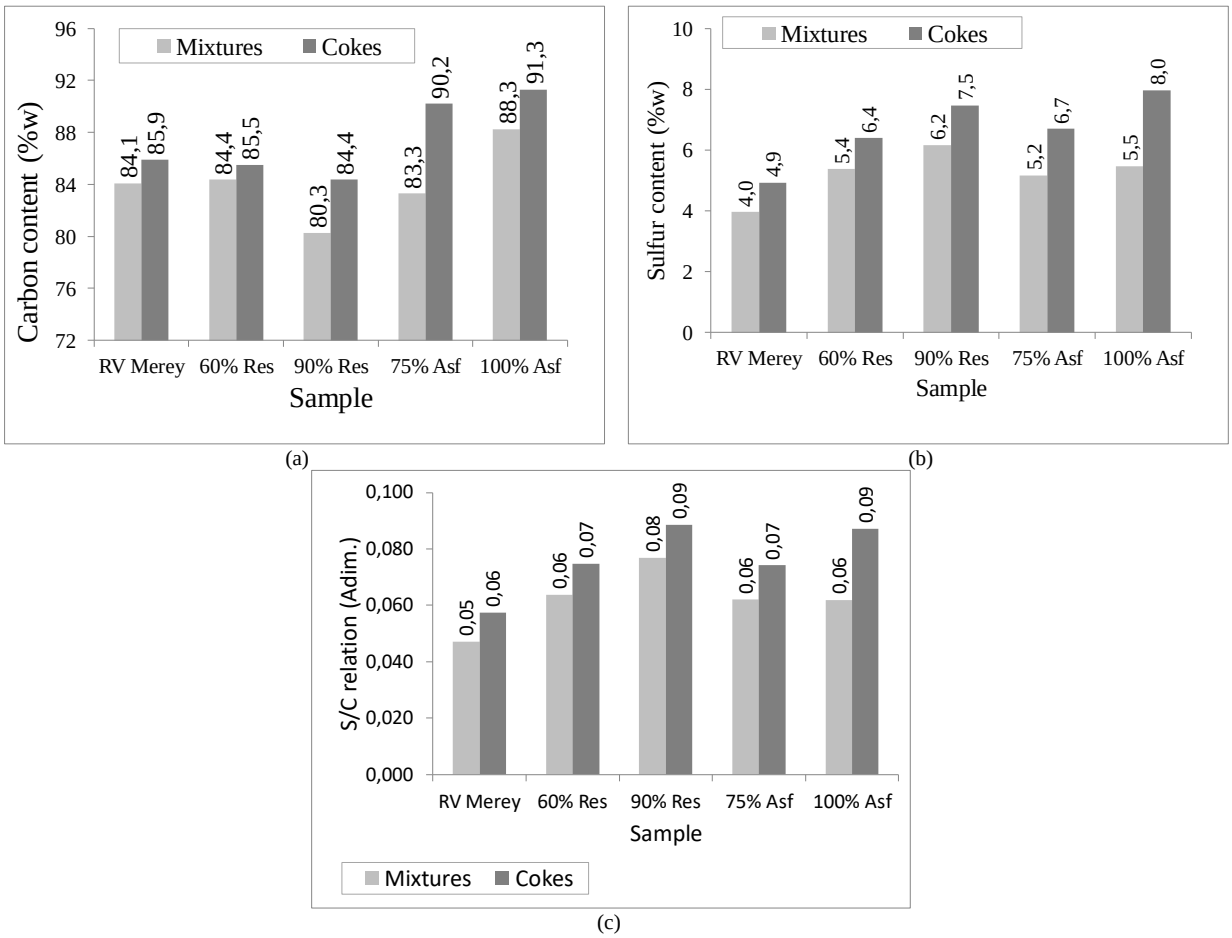

Figure 3. a) Carbon, b) sulphur and c) S/C relation of the studied mixtures and cokes

On analyzing the S/C relation (Fig. 3.c), it was found this parameter had a lower value in the Merey vacuum residue and greater in the resin and asphaltene rich mixtures. This finding shows that the extent of carbons substituted by heteroatoms in the resin and asphaltene rich mixtures is greater than the present in Merey vacuum residue, revealing an important role for sulphur within the chemical structure of the mixtures as they are more condensed. As a result, the same tendency was shown for the cokes from the delayed coking process as a consequence of its higher concentration of heteroatoms.

However, it is recommend that a more precise analysis of the C/H relation must be done to verify the studied samples condensation degree because the hydrogen content did not be measured by separately.In addition, the heavy metal content, specifically the vanadium and nickel (V y Ni) presents in Merey vacuum residue, of the prepared mixtures and the coke (C) obtained was determined (Fig. 4). As the amount of distilled collected was not enough for an analysis, on knowing the V and Ni content in the feed and in the coke, the amount of metal present in the distilled product (D) was found through a mass balance, .

Figure 4 shows the findings from the Merey vacuum residue, two resin rich mixtures (50 and 96 %w) and two asphaltene rich (75 and 90 %w) with the coke and corresponding distillate identified with the letters C and D. Showing an increase of the presence of metals in the feed and coke with the increase in the resin and asphaltene composition respectively, compared to the Merey residue.

The vanadium content increased considerably with the increase in the resin composition and did it even more with an increased in asphaltene fraction. This concurs with previous studies on the distribution of vanadium and nickel in hydrocarbon fractions and their variation in thermal processes which show that in terms of polarity distribution, most of the metals are concentrated in the resins and asphaltenes fractions (Liu *et al*., 2015).
Figure 4 also shows a greater concentration in the coke compared to the feed concentration which indicates, the metals remain trapped mostly in the solid product after the process. However, through a mass balance in the Merey vacuum residue and in the resin rich distillate, a considerable metal content, above 400 ppm, was found.
These findings do not concur with what was expected, the heavy metals should only be found in the coke. In the coking of these samples, it was evident that there was a drag of these metals toward the distilled product, mainly to the vanadium, which can be attributed to fluid dynamic problems existing in the coking reactor which causes part of the residue to be dragged by the distillates to the liquid product recollecting vial (Da Fonseca and Ruiz, 2014). In this case, on coking these mixtures, a projection of the

load toward the top of the reactor was produced and therefore there was no way to avoid the dragging of liquid and therefore obtaining metals in this product.

Nevertheless, on analyzing the results for the asphaltene rich mixtures, it was found that all the metal content which was initially concentrated in the mixtures became part of the solid products and so there was no dragging of metals toward the top of the coke reactor in these samples. Besides, the findings from the delayed coking of said mixtures showed in Nava (2017), indicate that the yield in distillates of the asphaltene rich mixtures was very low in all the cases (between 0.4 and 0.8 %w), confirming that the high asphaltene composition in the feed for the delayed coking process did not produce distilled products and therefore there was no dragging of metals.

From these findings, it is possible to conclude that as the resin composition increases, a coke with a higher concentration, mainly of vanadium, is obtained but with a lower concentration of nickel (the same occurs with metals present due to dragging in the distillates), while the increase in the asphaltene fraction, produces a coke with greater concentration of both metals which seems to indicate that the presence of vanadium is linked to the existence of both fractions in the mixture but in the case of nickel its presence could be linked only to the asphaltene fraction.

This inequity in the association between a certain fraction and the metal, could be linked to the existing differences in polarity of both fractions, with the asphaltene fraction being the most polar of the group of S.A.R.A. hydrocarbons (Speight, 2006; Zhang *et al*., 2013), which leads to one metal in particular joining a fraction and forming the typical organometallic compounds seen in previous studies.

The tendency obtained could be associated with the fact that the nickel content increases in the same way as the asphaltene content, and takes on a more important role, indicating that the fractioning could concentrate nickel in the more polar fractions. In the resin, porphyrinic nickel is distributed in the lighter sub-fractions of this hydrocarbons group while vanadium is distributed in the whole fraction (Liu *et al*., 2015). Therefore, the nickel acts as a substitute for the hydrogen in the asphaltene fraction and by being more polar, the metal content is more important for said fraction (Nava, 2017), and is thus also in the asphaltene rich mixtures and coke obtained from them .

III. CONCLUSIONS

The study showed that as resin and asphaltene content of delayed coking feed increases, the volatile material decreases and the fixed carbon, ash and metals in the vacuum residue increases, making it possible to modify the coke obtained characteristics . The carbon substituted degree by heteroatoms in the mixtures with high resin and asphaltene content is greater, showing the important role of sulphur within the chemical structure of these mixtures and the coke obtained.

Vanadium was found to be linked to both the resin and asphaltene fractions showing a higher concentration in the solid product from the delayed coking process, while nickel was found to be associated preferably with the asphaltenes and in this way is found in the coke.

It is recommend that the hydrogen content in the mixtures and the products obtained be measured to establish the C/H relationship and to verify the condensation level of the samples analyzed.

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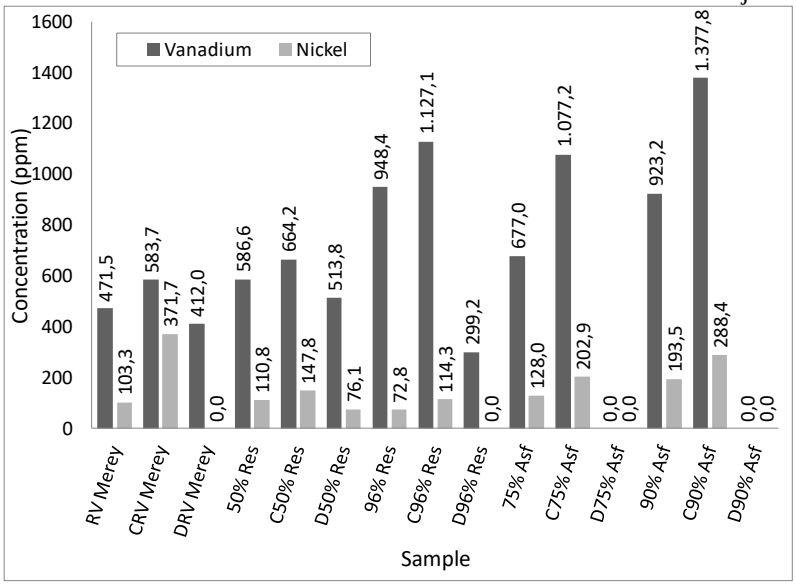

Figure 4. Concentration of metals in the mixtures, coke and distilled

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