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EFFECT OF RESIN AND ASPHALTENE CONTENT PRESENT ON THE VACUUM RESIDUE ON THE YIELD OF DELAYED COKING PRODUCTS

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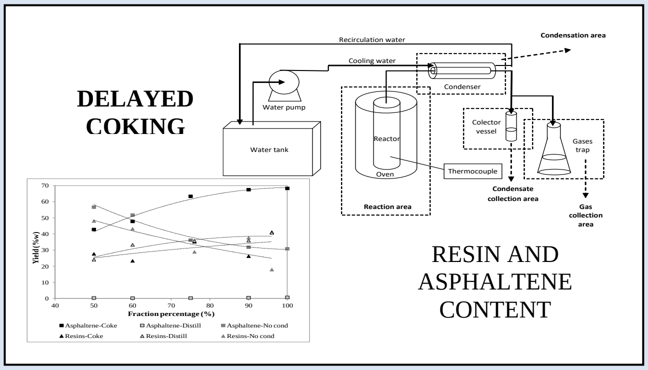

ABSTRACT

The effect of resin and asphaltene concentration in the feed, on the yield of delayed coking products was assessed, feeding controlled concentrations of the groups: saturates, aromatics, resins and asphaltenes (SARA) (50-100%w/w of asphaltene or resin and a fixed mass ratio of the others groups) prepared from a Venezuelan vacuum residue. The results of yield of products obtained in a laboratory-scale process show, that the increases of concentration of resins or asphaltenes raise yield of coke and decreases the not-condensable. The distillates yield remained at levels close to zero (<1%w/w) when asphaltene rich blends where fed, while in case of resin rich blends, the amount of distillate produced increased when the resins contents increased. These results are consequence of a higher condensation level of the molecules present in the crude. For distillates, a discriminatory behaviour occurred depending on in which fraction was rich the blend fed to the process, with yields in the order of 20-40% w/w for the mixtures rich in resins and practically equal to zero in the case of mixtures rich in asphaltenes.

Keywords: Resin, Asphaltene, Vacuum residue, Delayed Coking.

EFECTO DEL CONTENIDO DE RESINAS Y ASFALTENOS PRESENTE EN EL RESIDUO DE VACIO SOBRE EL RENDIMIENTO DE LOS PRODUCTOS DE LA COQUIZACIÓN RETARDADA

RESUMEN

Se evaluó el efecto de la concentración de resinas y asfaltenos en la alimentación sobre el rendimiento de los productos de la coquización retardada, a partir de la alimentación de mezclas de composición controlada de los grupos SARA: saturados, aromáticos, resinas y asfaltenos (50-100%p/p de resinas o asfaltenos y una relación másica fija entre los restantes grupos) que fueron preparadas usando como base un residuo de vacío venezolano. Los resultados del rendimiento de los productos, obtenidos en un proceso a escala laboratorio muestran que, el aumento en la concentración de las resinas o de los asfaltenos incrementa el rendimiento de coque y reduce el de los no-condensables. En cambio, el rendimiento de los destilados permanece en niveles cercanos a cero (<1%p/p) cuando se alimentan mezclas ricas en asfaltenos, y se incrementa cuando se alimentan mezclas ricas en resinas. Estos resultados son consecuencia del alto nivel de condensación de las moléculas presentes en el crudo. En el caso de los destilados, se observó un comportamiento discriminatorio dependiendo de cuál era la fracción mayoritaria en la mezcla alimentada al proceso, con rendimientos del orden de 20-40%p/p para las mezclas ricas en resinas y prácticamente iguales a cero en el caso de las mezclas ricas en asfaltenos.

Palabras claves: Resinas, Asfaltenos, Residuo de vacío, Coquización Retardada.

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1. INTRODUCTION

There are different types of treatments for heavy and extra heavy crude, being delayed coking one of the most widely used methods in Venezuela. The delayed coking process feeds itself mainly from vacuum residue, which is thermally treated so as to have two types of endothermic reactions occur, ones from cracking in order to obtain liquid and gas products and, others from polymerization-condensation where coke is obtained as a solid product [1].

This technology has been investigated since the 1950s, with the greatest amount of contributions in the 1970-1990s. In spite of this is a proven technology and the belief that new things cannot be obtained from it, authors like [2, 3, 4] look for to rescue the key role of this technology within the processes of refining, especially nowadays, when streams with a higher content of heavy fractions are being processed by the refineries worldwide.

In recent years, some works have been developed in the search to deepen into what happens within the coking process, since despite numerous investigations developed, not everything has been clear. Simulations [5, 6], proposals for kinetic models [7, 8, 9, 10] and prediction of yields of the products obtained [11, 12], try to establish those theoretical aspects that have not yet been elucidated.

In addition new trends on the use of other technologies to achieve improvements in the coking process have appeared, such as the use of additives [13], nanocatalysts [14] and the integration of processes or combined technologies that seek to take advantage of each one in order to obtain improvements in performance as in characteristics of the obtained products. The union of delayed coking with technologies such as [15]: deasphalting, gasification, ebullated bed, slurry phase hydrotreating, ultrasonic-assisted method [16] has shown to be beneficial for both, performance and the desired characteristics of the final products.

In the specific area of behavior of the key variables, works such as [17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29] show the influence of these on the yield and characteristics of the products obtained, for these new heavy and extra-heavy crudes that are being extracted from the subsoil in those countries such as the Venezuelan case, whose crude reserves have API gravities lower than the obtained in recent decades.

In previous works [23, 24], it was established the necessity of study the impact of crude oil constituent SARA fractions by separated, over the yield and the characteristics of products of delayed coking in general and in special for Venezuelan case, due to the narrow range of feed compositions that was studied in past [25, 26, 27, 28, 29], extending the evaluation range of the presence for each fraction in the feed [24].

From a laboratory scale study of delayed coking [23, 24] employing vacuum residues designed and constructed from heavy and extra heavy Venezuelan crude oils (with a high asphaltene proportion), it was evaluated the influence of the content and proportion of the SARA fractions and other basic characteristics like: volatile material, sulfur or heavy metals content, over the yield and quality of obtained products (coke, liquid and non-condensable). This constructed feeds that were rich in one of the hydrocarbon characteristic groups SARA, were prepared from three Venezuelan vacuum residues identified in based their origin as: Petrozuata, Amuay and Cardon, by means of the separation of their SARA fraction constituents, which were mixed maintained a controlled composition and higher to 50%w/w of each one of SARA fractions, generating the feeds denominated base-residuals.

These base-residuals were characterized in based on the C/H relation, immediate analysis, concentrations of heavy metals and Conradson Carbon, being that for those containing high concentrations of saturated and aromatic groups, C/H relation was lower, volatile material was greater, and the concentration of heavy metals and Conradson carbon were lower than in the case of residuum with higher concentrations of resin and asphaltene groups. Also it was obtained that the possibility of cracking and coke formation of the residuum, is directly related to the presence of the latter two groups in the crude oil [23]. Then, when the feeds were introduced in the coking process, the results show that an increment in yield of coke and gases, and a diminishing in yield of liquids, is obtained when the resins and asphaltenes concentration is incremented or aromatics and saturates concentration diminished. With regard to physicochemical analysis, it was observed that in all cases, the measured variables (C/H, metals, and sulfur content) change in an important way with increasing the presence of more polar and heavy fractions. The results correspond to the expected theoretical trends and show that each constituent group has a markedly different effect in the products obtained in the process [24].

These works [23, 24], although permit to evaluate the influence of the SARA groups from controlled composition feeds, did not achieve to evaluated the whole range of composition (intermediate values), reason why it was proposed to extract from a determined vacuum residue the constituent fractions and to extend the range of evaluation for the three more important group presents in the Venezuelan characteristic crude oil: aromatic, resin and asphaltene. The obtained results in the case of aromatics can be review in [30].

The general objective of this research was to evaluate the effect of the composition of resins and asphaltenes in the feed to the delayed coking process on the yield of the products, using a laboratory .scale. In order to fulfill this objective work was used an vacuum residue known as Merey. Merey is heavy crude of 16° API from Eastern Venezuela and from which ten blends were prepared: five rich in resin fractions and five rich in asphaltenes, to later on assess and relate the effect of this composition with the product yield obtained from the delayed coking process. The coking was carried out in a delayed coking unit at laboratory scale at the Carbon and Oil Residue Laboratory at Simon Bolivar University. In addition, the prepared blends were analyzed by means of Infrared Spectroscopy (IR) to identify the functional groups present and the existing differences in the intensity of the signals as a function of resins and asphaltenes presence.

This research intends to suggest improvements to the delayed coking process using Venezuelan crude and it aims to assess a profile of the resins and asphaltenes composition that will enable identifying the existing tendency between the composition of such fractions in the feed and yield of the products, this can be used by refinery planning units when making decisions in the selection of treatment strategies when the expected feeds have a high content of resins or asphaltenes.

2. METHODOLOGY

2.1 Residue separation in Saturates, Aromatics, Resins and Asphaltenes (SARA)

An SARA analysis was performed on the Merey vacuum residue following the ASTM D4124-09 norm [31] to identify its composition.

Afterwards, an SARA separation was done from the same residue by means of a greater scale method. Such separation was made aimed at obtaining enough quantity from every fraction of hydrocarbons that would enable for the preparation of blends with different percentages in weight of the SARA groups that will feed the delayed coking process.

The procedure to conduct the SARA separation from the Merey residue follows the methodology exhibited by [32]. For the precipitation of the asphaltenes, the method used by [33] was applied, using n-hexane as solvent, the residue was mixed with n-hexane in a 1:30 proportion, and the put into an agitation plate, to mix them for 6hrs, after which was filtered to separate the solid (asphaltene) and the liquid fraction (part of the maltenes). The solid fraction is washed in a soxhlet with n-hexane until the solvent was clear. The liquid remaining in the bottom was mixed with the before liquid fraction to conform the maltenes fraction, which was submitted to distillation to separate it from the solvent.

The maltene separation technique is a variation of the norm ASTM D4124-09 [31] and of the methodology developed by [34]. This norm (ASTM D4124-09) was selected because the similarity in characteristics, between heavy residue and asphalt. The method employed is based on the same adsorption and affinity principle with the solvents used in the norm ASTM D4124-09 [31], but 4 balloons are used as substitutes of the adsorption column, among which 25 g of alumina and silica gel were equally distributed, grade chromatographic, per maltene gram [23, 34], alumina in the first two balloons and silica gel in the last two were distributed.

The liquid obtained in the asphaltene separation after distillation, was mixed with n-hexane (1:150) and a portion of it was collocated in the first balloon shaking it for 2 min and leaving it in rest for 10 min. Then the supernatant was transferred to the next balloon, and put into the first balloon a new portion of the mix. Both balloons were then shaked for 2 min and leaving them in rest for 10 min. And so on with the rest of balloons until all the total mix maltene-n-hexane was transferred. The remaining liquid in the last balloon was reserved to separate after, the saturates fraction. This procedure was repeated with toluene (1:120) and a mixture 1:1 of toluene/methanol (1:120) to obtain the aromatic and resin fraction respectively. The remaining liquids in the three cases were collocated in a rotoevaporator to separate the three desired fractions from the solvents employed. An SARA analysis was done to the fractions obtained: asphaltene, first fraction obtained with n-hexane, second fraction obtained with toluene and third fraction obtained with toluene/methanol, according to the norm ASTM D4124-09 [31] to determine if they indeed correspond to saturates, aromatics, resins and asphaltenes.

2.2 Preparation for the delayed coking feeding process

The design of the mixtures consisted in construct 5 blends with a high content of resins and 5 with high content of asphaltenes, specifically between 50-100%w/w. The proportion between the remaining fractions was established as follow: in resin blends, 10%w/w of saturate fraction, 45%w/w of aromatic and asphaltene fractions; in asphaltene blends, 10%w/w of saturate fraction and 45%w/w of aromatic and resin fractions. This is for example, in a resin rich blend with 50%w/w of resin, the remaining 50%w/w correspond to 5%w/w of saturate fraction (10%w/w of the rest), and 22.5%w/w for aromatic and asphaltene fraction respectively (45%w/w of the rest). This design looked for maintain controlled relationship between the remaining fractions, but because it was not possible to obtain pure fractions (as it is shown later) the proposed blends were not achieved and the resulting blends are presented in table 1.

For the feeding process of delayed coking ten blends were prepared: five with high resin content and five with high asphaltene content. In the five blends with a resin representative composition, such fraction composition was varied between 50 and 96 %w/w, , (see Table 1). Is range was used due to the fact that the recovery of the fractions did not enable the obtaining of more than 96 %w/w of resins. For the preparation of such blends, the third fraction obtained with toluene/methanol was used as a basis to adjust the resins content and, in addition, a constant relation was maintained between the aromatics and asphaltenes content.

Table 1. Prepared blends for the delayed coking process.

Sample	*Saturates(%w/w)* ± σ	*Aromatics(%w/w)* ± σ	*Resins(%w/w)* ± σ	*Asphaltenes %w/w)* ± σ
1	21 ± 1	8 ± 1	50 ± 1	21.0 ± 0.1
2	17 ± 1	7 ± 1	60 ± 1	17.0 ± 0.1
3	9 ± 1	5 ± 1	76 ± 3	9.0 ± 0.1
4	4 ± 1	2 ±1	90 ± 1	4.0 ± 0.1
5	2 ± 1	2 ± 1	96 ± 1	0.0 ± 0.1
6	21 ± 2	8 ± 1	21 ± 3	50.0 ± 0.1
7	17 ± 2	6 ±1	21 ± 3	60.0 ± 0,.1
8	11 ± 2	4 ± 1	11 ± 3	75.0 ± 0.1
9	4 ± 2	2 ± 1	4 ± 3	90.0 ± 0.1
10	0 ± 0	0 ± 0	0 ± 0	100.0 ± 0.1

However, for the blend of 96 %w/w of resins it was not possible to adjust such a relation since any other arrangement among the fractions obtained made the resins content decrease to a percentage below 96 %w/w.

For the five blends with a representative composition of asphaltenes, the composition of this fraction was varied between 50 and 100 %w/w, (see Table 1) (σ represents the standard deviation of the experimental values). For the preparation of such blends, the fraction obtained forms the asphaltene precipitation was used as the basis to adjust the asphaltene content and, a aproximated constant relation between aromatics and resins content was maintained.

To guarantee homogeneity of the prepared blends, these were subject to a heating-shaking process with approximately 20 ml of toluene, slowly incorporating the corresponding quantity of each fraction. Once the sample is homogenized, the toluene was extracted based on the volatility difference.

Once the composition of the fractions at a greater scale was identified by mass balance, the mass required from each fraction was calculated to prepare the blends according with Table 1.

2.3 Delayed coking process at laboratory scale

The delayed coking was conducted in a laboratory scale unit located in the Carbon and Petroleum Residue Laboratory at Simon Bolivar University (see Figure 1) described in detail by [35].

Coking was conducted in a 0.7 x 12 cm, vertical reactor, presenting minor dimensions in comparison with the reactor used by Meza-Avila and collaborators [23], to try to reduce the drag of liquid fractions presented during the tests in the previous works [23, 24].

The operating conditions of the laboratory unit that were studied by [23, 24, 27, 28] were fixed to investigate only the feed composition effect. Employing a load of 2g, the variables used were: temperature 650 °C, reaction time 60 min, heating rate 5 °C/ min and 150 ml/ min of nitrogen as carrier gas. These operational conditions remained fixed for the thermal treatment of each blend. The start-up of the delayed coking unit was conducted as per the steps presented by [36].

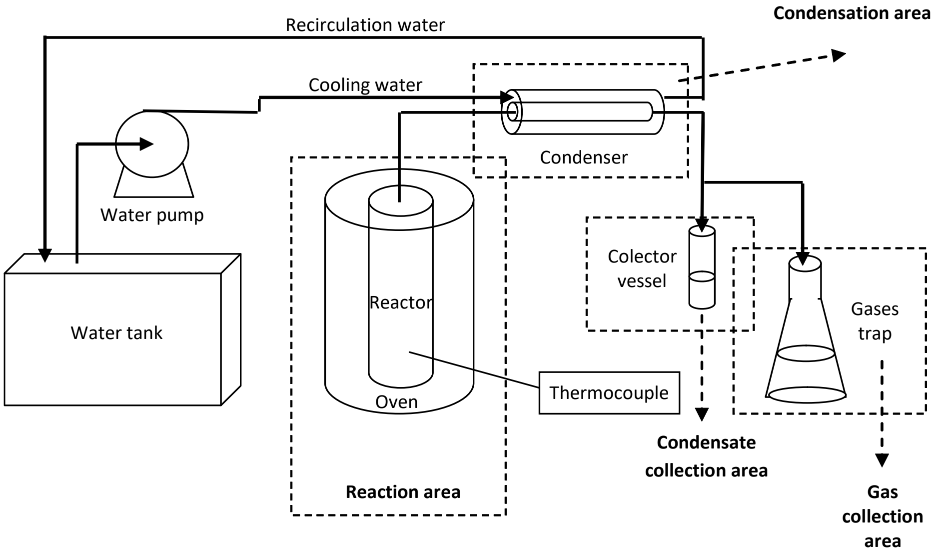

Figure 1. Delayed coking unit at laboratory scale [24].

2.4 Feeding Characterization to the delayed coking process

The fractions obtained from the SARA separation were subjected to the SARA analysis conducted at a greater scale through the Norm ASTM D4124-09 [31]. And the prepared blends were submitted to a functional groups identification by means of Infrared Spectroscopy (IR) using the ThermoNicolet iS5 iD5 ATR.

3. RESULTS AND DISCUSSION

3.1 Residue separation in Saturates, Aromatics, Resins and Asphaltenes (SARA)

Following the norm ASTM D4124-09 [31] and as of the SARA analysis of the Merey residue vacuum, 6.88 %w/w saturates, 23.32 %w/w aromatics, 46.22 %w/w resins and 23.57 %w/w asphaltenes were obtained [37, 38].

To conduct SARA separation at a greater scale of the Merey residue vacuum, the procedure proposed by [32] was used. A 23 %w/w percentage recovery was obtained for the asphaltene fraction. For the maltene separation the methodology was applied guaranteeing that the adsorbents were to be used immediately if their activation process was concluded. In Table 2 the recovery percentages of the maltene fractions obtained are shown.

Table 2. Fraction recovery from maltenes.

Fraction	*Recovery (%w/w)* ± *σ*
First fraction	24.0 ± 0.9
Second fraction	26 ± 2
Third fraction	50 ± 2

Once the fractions were obtained, an analytical SARA was conducted to know their composition and so minimize the error at the moment of preparing the blends to feed in the delayed coking process (See Table 3). It can be observed in Table 3 that an aromatic drag was obtained at the first fraction obtained with n-hexane and a resin drag at the second fraction obtained with toluene. These deviations in the maltene separations presented themselves due to a greater scale proceeding that does not enable maintaining the same relations between the alumina and the silica with the maltene grams used. Upon conducting the SARA analysis of each fraction following the norm ASTM D4124-09 [31], it was noted that the proportion between the alumina and the silica gel gram per maltene gram is around 500.

Table 3. SARA analysis results of the separated fractions.

Fraction	*Saturates (%w/w)* ± *σ*	*Aromatics (%w/w)* ± *σ*	*Resins (%w/w)* ± *σ*	*Asphaltenes (%w/w)* ± *σ*
First fraction	48.8 ± 0.4	45.3 ± 0.6	5.9 ± 0.5	0 ± 0
Second fraction	0.64 ± 0.07	84 ± 2	16 ± 1	0 ± 0
Third fraction	1.5 ± 0.2	3.0 ± 0.5	95.5 ± 0.9	0 ± 0

3.2 Delayed coking process at laboratory scale

Once the blends were prepared as it was explained before, they were introduced to the delayed coking process in laboratory scale. Figure 2 shows the yields obtained for the five prepared blends with a high resins and asphaltenes content respectively. The results are expressed for the coke, as well as the distilled and non- condensable products.

Figure 2 shows at a general level that the coke yield increased as the resins composition increased in the feeding of delayed coking process, a behaviour that was maintained for the distillates yield. On the other hand, the yield in non-condensable products decreased with the increase of resins composition in the blends.

For blends with a high content of asphaltenes, Figure 2 shows a more important increase of the yield in coke with the increase in composition of this hydrocarbon feeding fraction. For this group of blends, as the asphaltene content increased, a non-significant yield in distillates and a decrease in the yield of non-condensable products were obtained.

It was also possible to identify that the coke yield obtained for blends with a high content of asphaltenes resulted greater than that of the blends with high resin content, the same as that of the yield of non-condensable products.

These results correspond with the reported in previous studies, from where it was confirmed that the coke yield increases as the heavier fractions content increases (resins and/or asphaltenes) being the asphaltene content the most important for the coke formation, follows of the resins content [24, 39, 40].

Both fractions are mainly poly-aromatic hydrocarbons with aliphatic side chains that due to heat, break up or crack producing aromatic free radicals or poly aromatics of a smaller size, which can generate re-arrangements or molecular re-combinations by condensation producing hydrocarbons with poly-aromatic structures of greater weight and molecular size (poly-condensing), which are the preceding ones for coke formation [41]. Therefore, as their content increases at feeding, the greater the condensation will be among the poly-aromatic structures present, giving rise to the formation of a greater quantity of poly-condensing structures and encouraging coke formation.

In addition, a greater yield in gases and a minor one for the liquid products was obtained with the increase in the asphaltene content and an inverse behaviour for the case of resins content increase. This result shows that the asphaltenes preferably take the way of a greater intensity cracking of the outermost fractions which give rise to compounds of low molecular weight comprising the non-condensable products, followed by complete condensation reactions which give rise to a high coke proportion [42], while in the case of resins, the low-intensity cracking reactions generated by smaller molecules and the partial condensation reactions, from which the generated low-boiling aromatic compounds recombine causing a higher proportion of liquids and coke in the process, appear to be favoured in similar proportions [42].

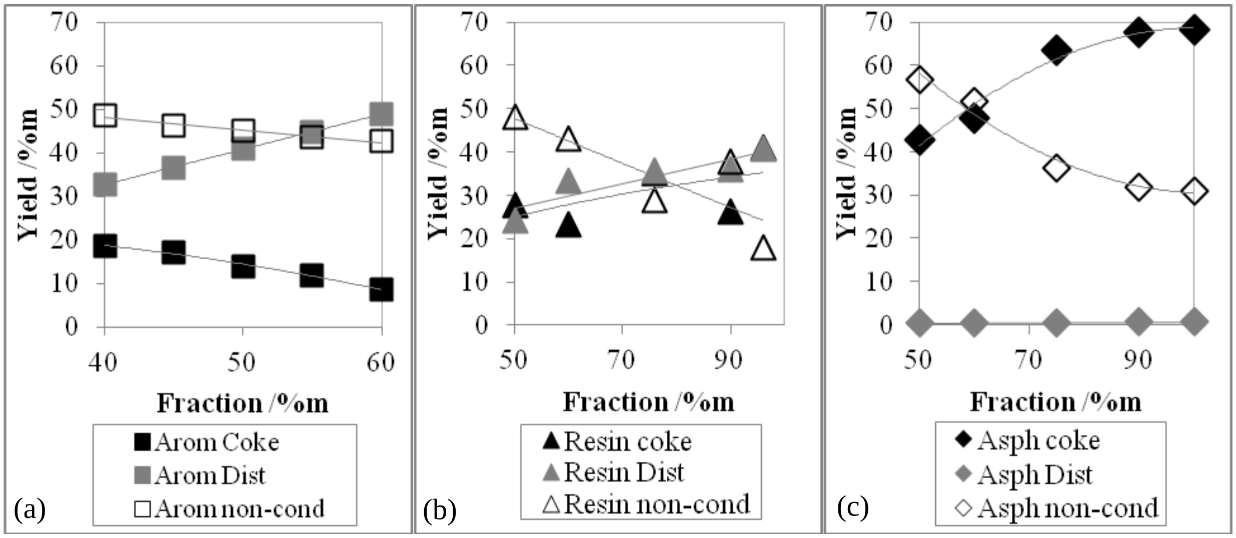

Figure 2. Yield of the delayed coking products for the prepared blends: a) Aromatics, b) Resins, c) Asphaltenes.

3.3 Feeding characterization to the delayed coking process

The method IR was conducted for 5 blends prepared with a high resins and asphaltene content. The spectra obtained were compared among each other to identify the present functional groups of resins and asphaltenes through the signals registered associated to these groups and the existing differences in the intensity depending on their composition in the blends. Figure 3 shows the spectra obtained for the extreme points of each group of blend.

From Figure 3 it can be observed that in all cases the same signals were obtained in the same ranges of wave numbers, which indicates the presence of the same functional groups for the blends rich in resins and asphaltenes correspondingly. For the blends with a high resins content it was noted that the spectra did not present representative differences due to the fact that the signals of blends with 50 and 96 %w/w overlap; however, there was a slight decrease (2-3%) in the wave intensity at 2923, 2852, 1456 and 1376 cm^{-1} with the increase in resin composition, which points at a minor presence of simple links due to more condensed blends with a higher resins content and a smaller content of saturates and aromatics.

Likewise, it was noted that for the rest of the signals (1700, 1600, 1020, 886, 812, 746 and 722 cm^{-1}) there was a slight increase (3-4%) in the intensity with the increase of the resins composition, which confirms a smaller presence of simple links and indicates a greater presence of links C=0, C=C, S=0 and aromatic condensations for such blends.

For the blends with high asphaltene content, greater differences between the intensity of spectra signals were identified (figures C and D). In this case, as the asphaltene composition increased and the one for the saturates, aromatics and resins decreased, there was a decrease in the intensity of signals to 2923, 2852, 1456, 1376 cm^{-1} , indicating a smaller presence of simple links. In regards to the rest of the signals there was also a slight decrease (2-3%) in the intensity of the signals. The obtained trend can be attributed to the complexity of such a fraction, which is more representative in the sample with 100 %w/w of asphaltenes; therefore, the arrangement, the distribution and in general, the contribution of this fraction together with the lower content of the rest of the fractions (S.A.R.), could have produced this small decrease in the signals as of 1700 cm^{-1}.

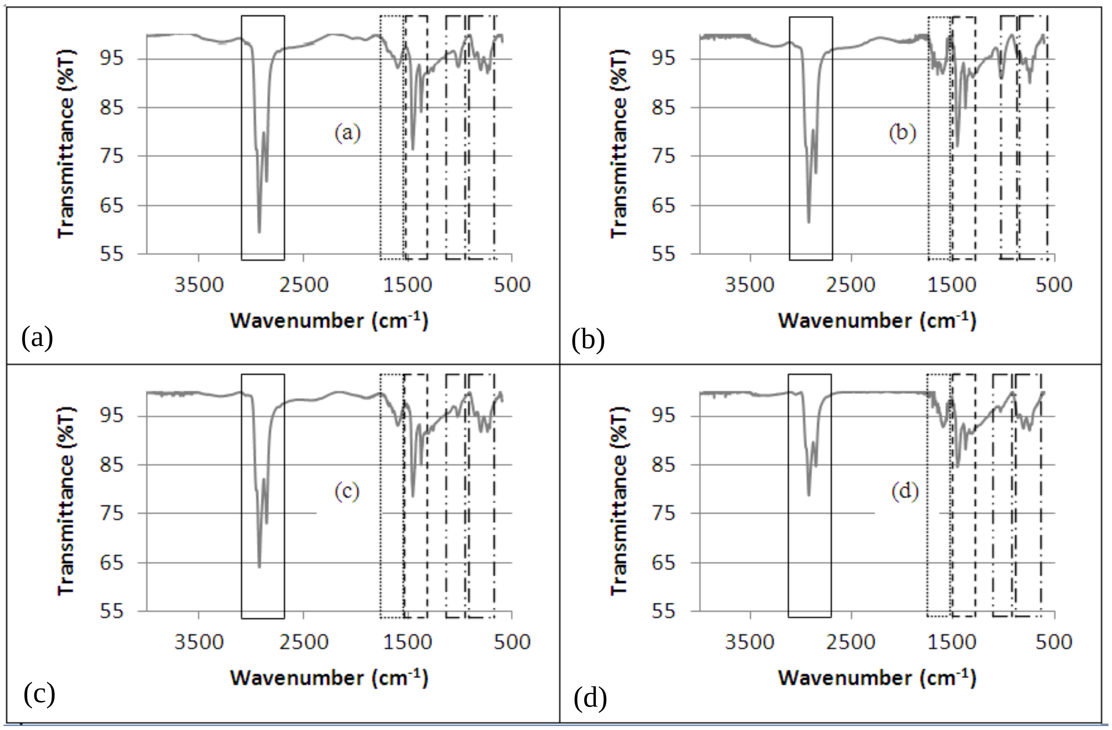

Figure 3. Infrared spectroscopy of the blends: (a) 50 %w resins, (b) 96 %w resins, (c) 50 %w asphaltenes, (d) 100 %w asphaltenes.

On comparing the spectra of the blends rich in resins and asphaltenes, in general it could be observed that for the blends with a greater content of resins a greater intensity was obtained for the signals 2923, 2852, 1456 and 1376 cm^{-1}, while with the analysis of the signals to 1700, 1600, 1020, and of 886 up to 722 cm^{-1}, it could be observed that such signals increase with the presence of a greater resins and asphaltenes content in the prepared blend, which indicates a greater presence of links C=O, C=C, S=O and aromatic condensations respectively.

Such trends were expected because as the blend is more condensed and has more complex fractions as resins and asphaltenes, the contribution of these fractions and their arrangement with the other fractions, makes the presence of simple links decrease as an increase in the presence of benzene rings, aromatics and heteroatom's condensations, which can influence directly in the yield and characteristics of the delayed coking products.

4. CONCLUSIONS

The study conducted enabled to identify that as the resin composition increases in the feeding to the delayed coking process, the coke and the distilled products yield increases. With the increase in the asphaltene composition a greater yield in coke is generated and a non-significant yield for distilled products, so that the increase of the asphaltene composition weighs negatively in the processes of thermal conversion, mainly due to the conversion yield to distillate products.

It is relevant to highlight this very low production of distillate of asphaltene rich blends that might suggest that the asphaltenes have a high preference to polymerization allowing only the outermost fractions of the molecule can be cracked to compounds of low molecular weight, which leave the process as not-condensable gases, disadvantaging the objective of the delayed coking process. In the case of the resins both reactions, polymerization and cracking, could occur in more similar proportions, giving rise to larger quantities of distillate as a product of the process.

The blends prepared for the delayed coking process showed the same functional groups, indicating a smaller presence in simple links and a greater presence of benzene rings, aromatics and heteroatom's condensations as the resins and asphaltenes composition increases in the blends typical with a high presence of these groups in hydrocarbons.

Experimental tests could be more effective in the reactions selectivity if they were done with a higher relationship between the grams of alumina and silica gel per maltene gram.

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