Simulation of the deasphalting process of crude oils: Models development and extraction conditions analysis

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ABSTRACT

Heavy crude oils are under constant investigation due to light oil exhaustion. So, its use is compulsory to meet the world energy demand. Heavy crude oils present several drawbacks as high content of metals, heteroatoms, and asphaltenes, and, therefore, upgrading processes are becoming essential. A deasphalting process, conventionally used for vacuum residue upgrading, can be an interesting pretreatment to eliminate the heavier phases and ease the crude processing in conventional refining facilities.

Most of the models developed for deasphalting simulation show problems to be implemented in simulation software packages. In this work, a versatile deasphalting simulation method is developed, composed by the definition of a synthetic crude oil model, formed by discrete pseudo components, and a deasphalting model approaching the process to a liquid-liquid extraction based on the thermodynamic model modified UNIFAC (Dortmund). Both models were satisfactorily validated. The deasphalting method was used to explore the solvent/crude ratio, extraction temperatures, and alternative solvents in substitution of conventional light paraffins. Higher extraction temperatures did not enhance remarkably the deasphalting process and the optimum solvent to crude ratio depends on the solvent type. Alcohols were found as promising compounds as their use is recommended by some studies and they showed great deasphalting results.

1. Introduction

The reduction of conventional crude oil reservoirs has led to an increase in the exploitation of heavy crude oils. So, the study of the effects of higher asphaltene content and the process to remove it has become very important (Mohammed et al., 2021). Within the refining process, deasphalting operation after the vacuum distillation leads to a heavy cut free of resins and asphaltenes, with reduced sulfur and metal content, and ready for catalytic cracking or hydrocracking, among other processes (Speight, 2020). The typical deasphalting process consists of a heavy feedstock upgrading step by the injection of light paraffins as propane, butane, or pentane into the vacuum residue. A heavy fraction formed essentially by asphaltenes is precipitated, eliminating contaminants as well as heteroatoms, metals, coke precursors, etc., and hence, upgrading the deasphalted oil (DAO) obtained that can be sent to further processes as Fluid Catalytic Cracking (FCC) or hydrocracking.

The deasphalting process is a complete mature technology included in most refineries, where four variations of the process can be found: Residuum Oil Supercritical Extraction (ROSE) licensed by Kerr-McGee,

the Demex process by UOP, the Solvahl process by Axens, and the Institut Français Du Petrol, and the Advanced Supercritical Deasphalting Process (PASD) by Petrobras. The differences of these deasphalting processes are found in the separation scheme, the solvent employed, temperature, and pressure, and their characteristics are wide detailed in the bibliography among with more variations with some improvements from the conventional processes (Ramirez-Corredores, 2017; Speight, 2020).

In the future, due to the increasing quality requirements of petroleum products, the deasphalting will become the main upgrading process for various feedstocks in refinery processes. In this respect, the use of deasphalting as a process before the atmospheric distillation for heavy crude oils can be an interesting approach. This would eliminate the heaviest phases, along with many contaminants, making easier the processing of the crude in the refining processes, such as catalytic ones. Furthermore, this approach would allow testing different conditions of the process like the temperature, solvent to crude ratio, or the solvent used.

Concerning the solvent used, some alternative ones have been

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considered for deasphalting in the refinery, as superheated water (Brons et al., 1993), N-methyl-2-pyrrolidone (Bushnell et al., 1977), dimethyl carbonate with CO_2 at overpressure conditions (Cesar Savastano and Cimino, 1993) and with sulfuric acid (Lerda et al., 1990). Furthermore, inside the well, more possible solvents have been studied for deasphalting as pretreatment before conventional refining. Ilyin et al. (2016) studied the amount of precipitated asphaltene and the final viscosity in relation to the solvent (paraffins, ethers, or HMDSO). Recent studies were focused on the use of propane or butane with additives within the reservoir (Rogel and Ovalles, 2013), the use of conventional solvents with solid particles of SiO_2 (Guzmán et al., 2017), acidic compounds that lead to the polymerization of asphaltenes (Sun et al., 2017), or using supercritical solvents as CO_2 (Nascimento et al., 2021). Their objectives are the improvement of the standard process by increasing the sulfur and metal reduction (Guzmán et al., 2017), solvent recovery, and reducing energy consumption (Ahn et al., 2016). Nevertheless, none of these works have studied the use of less hazardous solvents. Some studies (Byrne et al., 2016; Prat et al., 2014, 2015) have developed technical criteria to recommend the use of alternative solvents in chemical industry. Alcohols, esters and ketones appear in these recommendations since health, safety and environmental concerns are reduced compared to conventional ones. The use of alternative and recommended solvents in deasphalting appears as a new field to study.

The study of the deasphalting with experimental work is necessary but laborious and time-consuming. The addition of simulation experiments appears as a useful alternative to reduce the time and resources of experimentation. The simulation of such a process implies, first, the need of model crude oils, whose composition and components distribution are complex and variable for every crude oil type. Secondly, the deasphalting separation is based on molecular types differences between the precipitated and the remaining phases of the DAO, unlike most of the separations in the refinery, based on the boiling point gradient. These aspects hinder the simulation of the deasphalting process in simulation software packages.

For a long time, several models have been applied to describe the asphaltene solubility and precipitation, but only a qualitative agreement was found, where models incorporate molecular weight distribution and distributions of solubility parameters of solutes as the most important data (Andersen and Speight, 1999). Some authors use semi-empirical models where these parameters are considered (Fahim, 2007; Nunes et al., 2019; Painter et al., 2015) and recent studies are found that support the use of empirical models over other ones (Santos et al., 2019). In contrast, other authors use thermodynamic models with specific modifications for asphaltene solubility. For example, models with a modification of the Flory-Huggins polymer theory (Wang and Buckley, 2001) and the Kikic modification of the Flory-Huggins theory (Santos et al., 2017) are found. The Peng-Robinson equation of state for the simulation of several upgrading units, assuming liquid-liquid equilibrium (LLE) for the deasphalting unit is also used (Gholami et al., 2021). As well, the regular solution theory and the assumption of LLE between the asphaltenic and non-asphaltenic phases is assumed to simulate the process (Tharanivasan et al., 2009). A recent work (Daryasafar et al., 2020) found better modeling results usinga more complex thermodynamic model as perturbed-chain statistical associating fluid theory (PC-SAFT).

Most of the above models describe quite accurately the asphaltene behavior. However, they are limited to specific crude oils and conditions, and their accurateness is directly related to their complexity. Therefore, their implementation in simulation software packages and within the rest of the refinery models is a gap to fill. To our knowledge, there is not described a straightforward and versatile method to use in simulation software packages that work correctly.

This work focuses on the option to carry on a deasphalting process during the refining process before the atmospheric distillation and the optimization of such process using simulation. The aims of this work are, first, to develop a tunable model (synthetic crude oil model -SCO-), to define any crude oil with specific pseudo components, allowing its use with group contribution thermodynamic models, and validate it with experimental data of real crude oils from literature. Second, to develop a straightforward and versatile model based on the LLE fundamentals to simulate the deasphalting process implemented in Aspen Plus®, and validate it by two steps: with experimental data literature, on the one hand, and experimental results from this work, on the other hand. Finally, the simulation method, combining the SCO and the deasphalting models, is used to test different conditions of the deasphalting process, combining both models: the use of alternative solvents, solvent to crude ratio, and temperature of deasphalting.

2. Synthetic crude oil model

2.1. Crude oil model development

The tunable synthetic crude oil model (SCO) was developed emulating a medium-heavy crude oil, whose properties were compared with experimental data of Maya (heavy) and Istmo (light) oils (Espinosa-Peña et al., 2004). The elemental and structural compositions were also calculated and compared with the bibliography (Iwase et al., 2018).

The use of the SCO for deasphalting modeling implies the separation by molecular type (asphaltenic/non-asphaltenic). For this purpose, the saturates, aromatics, resins, and asphaltenes (SARA) families distribution was employed and it was set according to the literature (Fulem et al., 2008; Zhao and Shaw, 2007): 30% saturates, 50% aromatics, 5% resins and 15% asphaltenes, in mass basis. The SCO was formed then by discrete pseudo components where thirty molecules were included: nine saturates, ten aromatics, five resins, and six asphaltenes. Mass fractions of individual molecules were equally divided within their family. Fig. 1 shows one example of each SARA molecule. All the molecules included can be consulted in supplementary materials.

Table 1 shows the boiling point, calculated by the Gani equation (Constantinou and Gani, 1994), and molecular weight of the molecules estimated, sorted by SARA families, and ordered by boiling point. As can be seen, the SCO includes molecules covering a wide range of properties including asphaltenes molecules that are big enough to represent the heavy fraction, whose shape of all of them can be consulted in supplementary materials.

Heteroatoms (Nitrogen, Sulfur, metals) have not been considered since their presence does not affect the process.
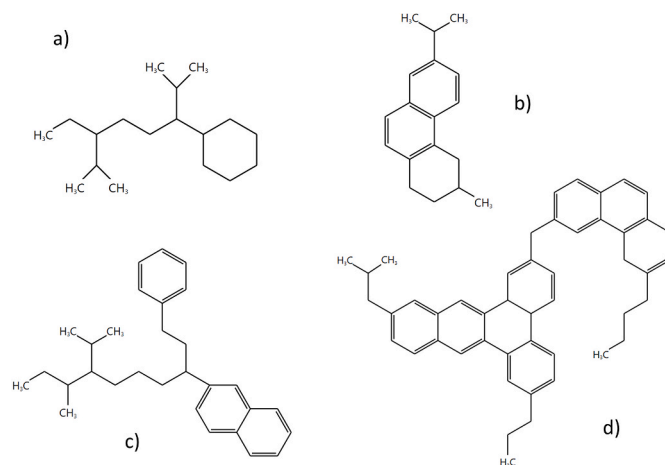

Fig. 1. Examples of some molecules of the SCO. a) saturate; b) aromatic; c) resin; d) asphaltene.

Table 1

Properties of the pseudo components of the synthetic crude oil.

Family	Molecules	Boiling point (°C)	Molecular weight (g·mol^{-1})
Saturates	1	133.5	114.2
	2	164.8	128.3
	3	167.8	140.0
	4	236.9	212.0
	5	277.6	252.0
	6	278.9	254.0
	7	321.8	282.6
	8	369.4	381.0
	9	404.9	422.8
Aromatics	10	138.2	106.2
	11	222.0	176.0
	12	234.8	174.3
	13	297.9	212.3
	14	308.4	256.4
	15	315.7	270.4
	16	319.0	240.4
	17	326.6	238.4
	18	347.2	298.0
	19	350.9	314.0
Resins	20	354.9	312.0
	21	407.6	400.6
	22	427.0	454.7
	23	447.0	490.0
	24	465.4	504.8
Asphaltenes	25	502.8	588.9
	26	516.5	564.8
	27	521.3	638.9
	28	524.8	626.0
	29	527.6	607.0
	30	550.5	719.0

2.2. Characterization and validation of the SCO model

Once created the SCO, its TBP curve, and API gravity were estimated by Aspen Plus®, among the rest of the properties, and validated with experimental data from literature [23,24]. The validation of the SCO model was first made comparing the TBP curve of the SCO, calculated by Aspen Plus® software, and the literature values of the Istmo and Maya crude oil samples (Espinosa-Peña et al., 2004), showed in Fig. 2. The calculated TBP is similar to the experimental ones. The literature does not show more than 80% distilled, but the final tendency of the SCO with a slope increase is the usual one because of the asphaltenic fraction.

The API gravity of the SCO resulted in 28 °API. If compared with the experimental API of the Maya (<20°API) and Istmo oils (<30°API) (Espinosa-Peña et al., 2004), the SCO model is similar to the Istmo crude
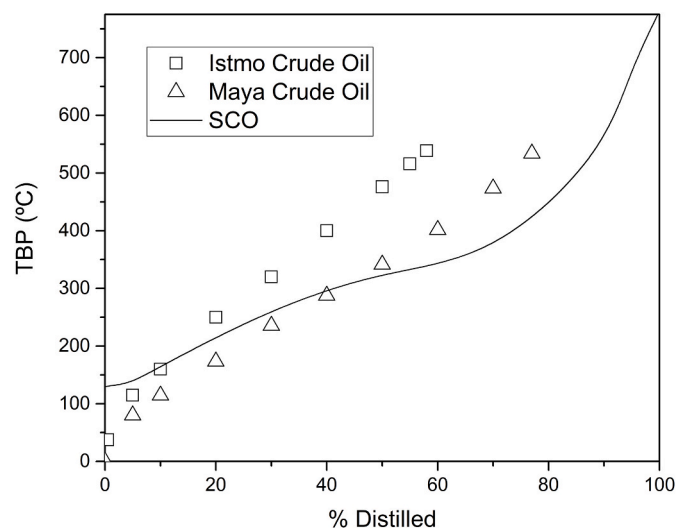
oil, and, concerning this property, classified as intermediate crude oil model.

Table 2 lists the resulting elemental and structural composition of the SCO model and the comparison with bibliographic data. Bibliography (Iwase et al., 2018) considered different compound families (saturates, lost components, aromatics, and resins) and next correspondence between SARA and such bibliographic families was established: SARA saturates as saturates, SARA aromatics as lost components, SARA resins as aromatics, and SARA asphaltenes as resins. A final comparison of the SCO values with the bibliographic ones was carried out considering the sum of saturates and aromatics compounds as the light fraction and the sum of resins and asphaltenes as the heavy fraction. The validation of these parameters can be considered more realistic for deasphalting modeling.

The comparison of the values serves to check a correct composition of the SCO as an average intermediate crude oil. In main terms, SCO and references fit adequately, which means that the molecular weight and composition of the SCO molecules are correctly estimated. However, since the SCO was not developed to be a duplicate of the literature values (Iwase et al., 2018), some deviations appear.

The aromatic content of the SCO is higher than that of the literature. Given that the SCO is heavier in terms of asphaltenic proportion, its aromaticity is increased. In the heavy fraction, the aliphatic content of the SCO is mainly due to small branches rather than large chains, methyl-branched or naphthenic carbons, as the values indicate. Concerning the structural composition in the aliphatic content of the SCO, the values are lower, but proportionally, they fit with the bibliographic values. The rest of the values do not show large deviations and for individual structural groups, the standard deviation (σ) between calculated and bibliographic values is 6.6%. The standard deviation was calculated as the square root of the average of the squared differences of bibliographic and calculated values.

From the results shown above, the SCO model is characterized and validated. Moreover, the SCO can be modified to represent other crude oils according to the modeling requirements by adjusting the composition of the SARA groups, the individual compositions or even adding new molecules, which gives versatility to the model. Nonetheless, we remark that the simplification of the SCO by not including heteroatoms in the molecules should not have a strong effect on the thermodynamic

Fig. 2. Total Boiling Point distillation curves.

Table 2

Elemental and structural composition of SARA families of this work and bibliographic data.

	Saturates + Aromatics		Resins + Asphaltenes		SCO	
	Model	Bibl. (Iwase et al., 2018)	Model	Bibl. (Iwase et al., 2018)	Model	Bibl. (Iwase et al., 2018)
Mole fraction (%)	90,6	88,8	9,4	11,2		
Mn (g/mol)	234	265	576	480	302	306
Ratio C/H (%)	87,9	88,0	91,1	88,8	88,5	88,1
Total Aromaticity Content (%)	27,1	21,6	60,6	55,8	30,2	25,4
Total Aliphatic Content (%)	72,9	78,4	39,4	44,2	69,8	74,6
Other aliphatic (%)	25,4	28,3	22,3	10,8	25,1	26,3
Chain CH$_2$ + Aliphatic CH (%)	25,6	23,9	8,5	17,2	23,9	23,1
Total α-CH$_3$ + β-CH$_3$ + γ-CH$_3$ (%)	16,0	18,6	7,4	12,8	15,2	17,9
Naphthenic CH2 (%)	5,9	7,7	1,3	3,1	5,5	7,2

model selected, however, for further works, the incorporation of heteroatoms in the molecules, whenever the binary parameters are available, would serve to confirm this fact and manage a more realistic model.

3. Deasphalting model

3.1. Thermodynamic model

In this work, the deasphalting process was approached to an LLE. The model uses the LLE Eqs. (1) and (2):

$$f_i^\alpha = f_i^\beta \tag{1}$$

$$(x_i \gamma_i)^\alpha = (x_i \gamma_i)^\beta \tag{2}$$

where x_i, f_i, and γ_i are the molar fraction, fugacity, and activity coefficient of component i, and superscripts α and β represent the two liquid phases.

A predictive thermodynamic model would be the best option to calculate the activity coefficients due to the variable nature of the molecules. In this sense, the group contribution methods are very powerful models that can be applied to any molecule. The most used ones for activity coefficient calculation are the UNIFAC (Fredenslund et al., 1975) and its variations: mod. UNIFAC (Dortmund) (Constantinescu and Gmehling, 2016), mod. UNIFAC (Lingby) (Larsen et al., 1987), etc. The mod. UNIFAC (Dortmund) has been demonstrated to give better results than the rest of the models (Gmehling et al., 2015), mainly due to its improvement in the temperature dependence of the group interaction parameter. Furthermore, its parameters matrix data have been updated regularly during the last years according to new experimental information in the Dortmund Data Bank. Therefore, the mod. UNIFAC (Dortmund) was the thermodynamic model selected.

The deasphalting process was simulated in a one-stage LLE extractor using Aspen Plus® software, as schemed in Fig. 3. The SCO and the solvent are the inlet currents to the LLE extractor. Two equilibrium phases are obtained as outlet currents, an asphaltenes rich phase (ARP) that contains the highest quantity of resins and asphaltenes, and a solvent rich phase named deasphalted oil (DAO), keeping most of the light fraction (saturates and aromatics).

The comparison of the deasphalting results was carried out according to two criteria:

- The asphaltenes reduction in the DAO and the extraction yield.
- The partition coefficients and the selectivity.

The first two parameters are commonly used as parameters of the deasphalting processes. The asphaltene reduction parameter stands for the mass quantity of the heavy fraction that is eliminated from the SCO forming the ARP phase, and then, when it is higher, the quality of the DAO improves. The extraction yield represents the efficacy of the DAO obtention, and its optimal is the sum of the content of the SCO light fraction (when asphaltene reduction is 100%).

The second criteria of parameters are widely used in liquid-liquid extraction processes. A partition coefficient indicates how one or some

Fig. 3. LLE extractor simulation scheme.

substances are distributed between the two liquid equilibrium phases. Finally, the selectivity helps to know if a solvent extracts specifically a target substance, or a group of substances, of the multicomponent mixture, or if it extracts several substances non-selectively. With both parameters, a solvent screening can be carried out to select one for an extraction process design. Such magnitudes are calculated by Eqs. (3)–(7).

$$AR(\%) = \frac{(W_{R+A})^{ARP}}{(W_{R+A})^{SCO}} \cdot 100 \tag{3}$$

where AR is the asphaltenes reduction (%), (W_{R+A}) is the mass flow of resins and asphaltenes and ARP and SCO superscripts refer to asphaltene rich phase and synthetic crude oil currents, respectively.

$$y_E(\%) = \frac{W^{DAO}}{W^{SCO}} \cdot 100 \tag{4}$$

where y_E is the extraction yield (%), W is a mass flow current (solvent not counted) and DAO superscript refers to deasphalted oil current.

$$S_H = \frac{K_H}{K_{DAO}} \tag{5}$$

where S_H is the selectivity, and K_H and K_{DAO} are the partition coefficients of the SCO heavy fraction and DAO light fraction, respectively, as determined by the following equations:

$$K_H = \frac{(x_{R+A})^{ARP}}{(x_{R+A})^{DAO}} \tag{6}$$

where K_H is the partition coefficient of the SCO heavy fraction, (x_{R+A}) is the molar composition of the resins and asphaltenes.

$$K_{DAO} = \frac{(x_{S+Ar})^{ARP}}{(x_{S+Ar})^{DAO}} \tag{7}$$

where K_{DAO} is the partition coefficient of the SCO light fraction, (x_{S+Ar}) is the molar composition of the saturates and aromatics.

3.2. Validation of the deasphalting model

The validation of the deasphalting model was carried out in two steps. The first one consisted of a benchmarking between the simulated and experimental data of LLE extractions of aromatics, from mixtures of saturates and aromatics compounds. The experimental data of the LLE extractions were obtained from the literature (Al-Jimaz et al., 2005; Alkhaldi et al., 2009; Fandary et al., 2006). Table 3 lists the five systems selected for the validation, including all the compounds involved in each system, the solvent, the extraction temperatures, and the bibliographic references.

The parameters analyzed were the compositions (mole fraction) of the saturates, aromatics, and solvent at each equilibrium phase, selectivity S_H (Eq. (5)), and the partition coefficient K_H (Eq. (6)). Fig. 4 shows the comparison between the experimental and the simulated results of some of these parameters for systems 3, 4, and 5 (Table 3). Since these systems carry out the extraction of aromatics at low concentrations, there is a solvent-rich phase that contains the largest content of aromatics (ARP), and the saturates remain mostly in a saturates rich phase (DAO). In Fig. 4, it is observed that the simulated and experimental results mostly agree within the point clouds. Nonetheless, the deviations appreciated are mostly due to the compositions of the solvent and the saturates, since their compositions are noticeably higher than the aromatics ones, leading to higher deviations in absolute terms, which does not mean that the relative errors are higher. Furthermore, some tendencies of the deviations of the saturate and the solvent are visualized in both DAO and ARP phases, which are caused by the error committed by the mod. UNIFAC when the LLE is calculated and leading to a
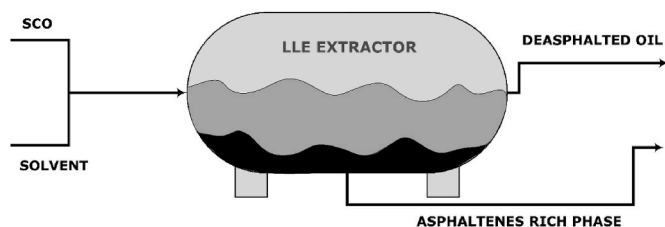
Table 3

Data of the materials and their experimental works selected for validation of the model.

| System	Compounds		Experimental conditions		
	Saturates	Aromatics	Solvent	Temperatures (°C)	Reference
1	n-Dodecane and n-hexadecane	Mesitylene and n-butylbenzene	NMP	20, 30	Alkhaldi et al. (2009)
2	n-Tetradecane	Pentylbenzene	NMP	24.85; 34.85; 44.85; 54.85	Fandary et al. (2006)
3	n-Dodecane	Propylbenzene	NMP	24.85; 34.85; 44.85; 54.85	Al-Jimaz et al. (2005)
4	n-Tetradecane	Propylbenzene	NMP	24.85; 34.85; 44.85; 54.85	Al-Jimaz et al. (2005)
5	n-Heptadecane	Propylbenzene	NMP	24.85; 34.85; 44.85; 54.85	Al-Jimaz et al. (2005)
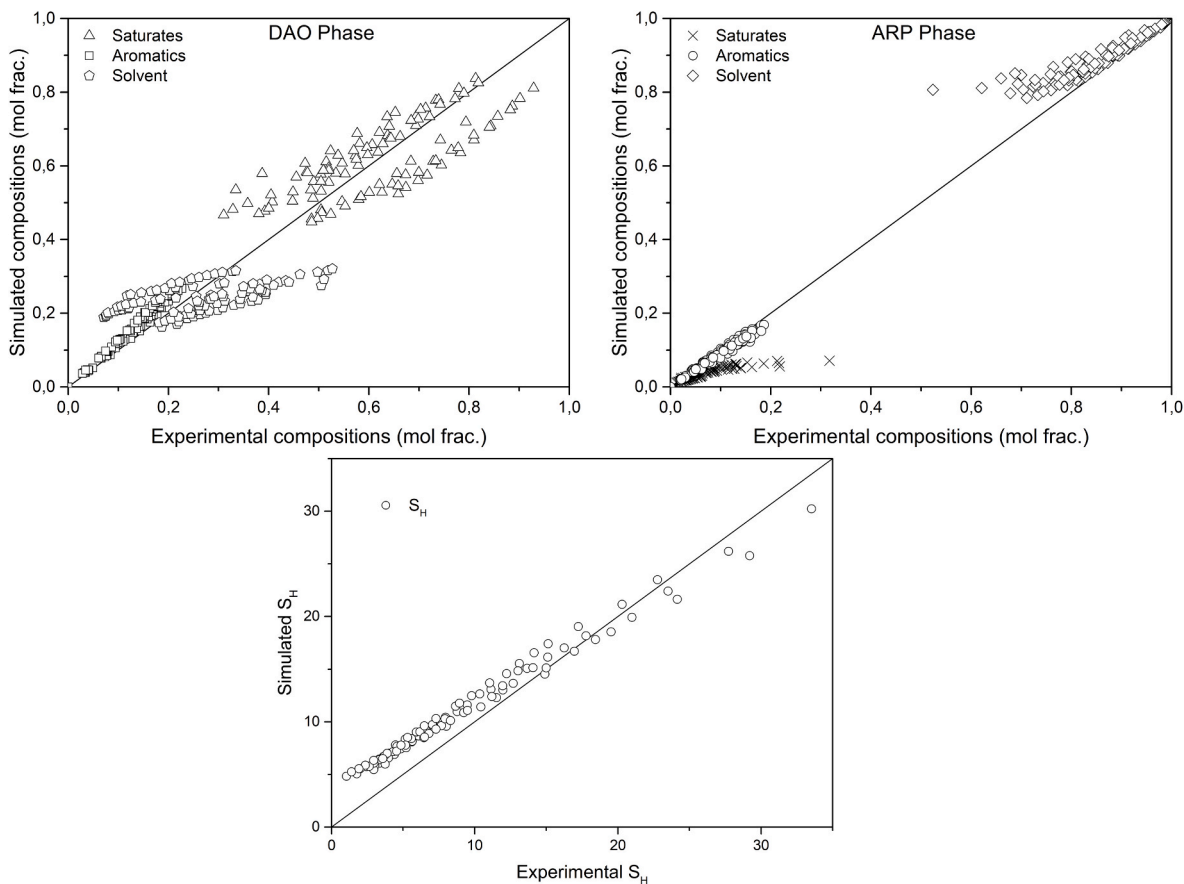
Fig. 4. Experimental (Al-Jimaz et al., 2005) vs simulated mole fractions for ARP and DAO phases and selectivities (S_H) of the reference systems 3, 4, and 5 of Table 3.

displacement of the phase coexistence region, which drags the tendency of the deviation in the selectivity as well.

Table 4 shows the quantitative analysis of this validation, wherein the standard deviation and the maximum values observed of the compositions (of each family and extraction phase), partition coefficients

Table 4

Full model validation: standard deviations (σ) and respective maximum values observed (Max. value obs.) for each SARA family and extraction phase (mole fraction), partition coefficient, and selectivity.

		σ	Max. value obs.
Deasphalted Oil	$X_{SATURATES}$	0.112	0.935
	$X_{AROMATICS}$	0.031	0.228
	$X_{SOLVENT}$	0.093	0.527
Asphaltene Rich Phase	$X_{SATURATES}$	0.061	0.318
	$X_{AROMATICS}$	0.019	0.187
	$X_{SOLVENT}$	0.078	0.988
	K_H	0.245	1.288
	S_H	4.638	33.52

(K_H), and selectivities (S_H) are presented. The maximum values observed give an idea of the relative significance of the standard deviation of each case.

Small deviations appear between the model and the experimental data, so the deasphalting model predicts correctly the LLE extraction of the aromatics of the systems. The standard deviations are not remarkable respect to the maximum values observed, which indicates that the model results are correct. Moreover, if the temperature effect on the deviations was calculated, a tendency of increasing errors when extraction temperatures get higher would be observed, being the smaller phase coexistence region at higher temperatures as the possible reason behind this fact.

The second validation step was performed in our laboratory and it consisted on the benchmarking with an experimental deasphalting, carried out through asphaltene precipitation with isopropanol of a Maya crude oil following the standard test method IP 143 (Energy Institute, 2016). This standard allows precipitating C_7-asphaltenes of a crude oil, isolating as well the saturates, aromatics, and resins by means of a multistage solvent extraction with n-heptane and toluene. In this work, n-heptane was replaced by isopropanol to validate the model with a

solvent that we are going to analyze and the literature endorses its use as a solvent (Byrne et al., 2016; Prat et al., 2014, 2015). Maya crude oil sample was supplied by Repsol S.A. and isopropanol (100%) purity by VWR.

The extraction yield was calculated for experimental deasphalting and the corresponding simulation at different R–S/C ratios (Fig. 5). The Maya crude oil is viscous enough to heavily hinder the experiments at R–S/C lower than 5, so that, trials at R–S/C 2 and 3 did not show satisfactory results due to massive sample mass loss. Therefore, the onset region was not determined completely. However, the rest of the experiments ran correctly at R–S/C 5, 10, 20 and 30, by triplicate. From R–S/C 5 onwards, the experimental y_E sets constant, despite a low descent that we attribute it to experimental uncertainties. Secondly, the simulated y_E does not stabilize until around R–S/C 30, and a slight overestimation of the y_E by the model is detected for R–S/C over 5. However the standard deviation between all the experimental and simulated y_E was 4.44% and consequently, the deasphalting results from the simulation are considered acceptable, and the model validated.

Nevertheless, this model only contemplates the LLE as the separation mechanism of the deasphalting, however, the deasphalting is far more complex, including solid-liquid equilibria and the destabilization of the asphaltenes when the solvent is added, producing flocculation and the final precipitation of these molecules. The validation confirms that the LLE is a satisfactory estimation for the solvents tested in this work, nevertheless, we suggest that future research should be made concerning the incorporation of these precipitation mechanisms into the simulation software package without worsening the versatility of the model.

4. Analysis of the deasphalting conditions

Once validated the SCO and the deasphalting models are combined to study different deasphalting conditions. The variables analyzed were: solvent to crude oil ratios (values ranging from 1 to 30), extraction temperature (set at 20 and 50 °C), and some alternative solvents. Related to the solvent selection, we considered technical criteria (risk, health, environment, quality, industrial constraints, and cost) (Prat et al., 2014), and ten solvents were selected: four aprotic polar ones, four alcohols, and two esters, covering a wide range of solvent types. Table 5 summarizes their boiling points and use recommendations.

4.1. Solvents selection

The analysis of the solvents selected was carried out, wherein the y_E, AR, S_H, and K_H served to rapidly find the most interesting solvents in a
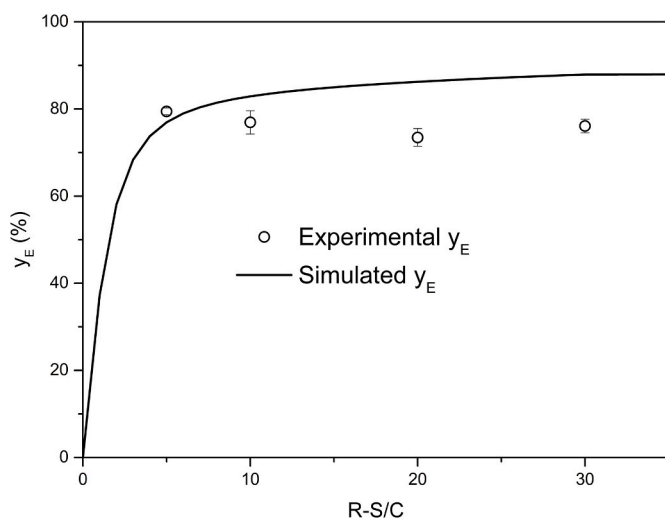
Fig. 5. Validation of deasphalting model through experimental deasphalting.

preliminary selection. Fig. 6 plots the best results for each solvent for all the R–S/C (20 °C), where the most suitable ones are found at the top-right side of both plots.

Fig. 6 a) shows a conventional solvent screening for solvent extraction (K_H and S_H). The solvents line up as seen, being the methanol optimal, followed by the rest of the alcohols, then, the polar aprotic solvents, and finally, the esters. Fig. 6 b) shows the solvents' results in terms of extraction yields and asphaltene reduction. Three main zones can be found, the first in which some alcohols proposed as the best solvents (methanol, isopropanol, and tert-butanol) with an average y_E of 78% and AR of 84%. Methanol reaches a better position in Fig. 6, but it needs an R–S/C 30. Tert-butanol and isopropanol produce worse AR but higher y_E in most cases and for an optimum R–S/C of 4–5. Thus, they need 7 times less amount than methanol at their optimum point, so this lower R–S/C would allow a lower use of solvent. Further experimentation and a techno-economic assessment are needed to confirm the goodness of these solvents for deasphalting use and to discard potential problems.

The second zone corresponds to three of the polar aprotic solvents (DMF, NMP, and DMA) with y_E of 67% and AR of 44%. These solvents have particular behaviors, and their high boiling points represent an interesting advantage. Moreover, they serve usually as aromatic selective solvents, so we think they need a deeper study to check their potential use. Eventually, their great disadvantage is that they are not recommended because of their dangerousness (Prat et al., 2014). The third zone is formed by ethylene glycol and sulfolane, with a y_E of 19% and AR of 94%, so they would not be favorable for this process with these conditions. The esters stay apart of these zones, being discarded for deasphalting due to their poor results.

Some differences between the K_H-S_H and y_E-AR criteria are observed. They lead to consider that K_H-S_H calculation for solvent screening for the deasphalting process is not adequate. The reason is that the optimal solvents selected with this criterion are not eliminating the asphaltenic fraction significantly. Therefore, we think that y_E-AR criterion is better to evaluate the deasphalting.

Finally, the typical industrial extraction yields with light paraffins are stated at 56 ± 9% and also total AR (Speight, 2020). Besides, the experimental y_E of the Maya crude oil with isopropanol in this laboratory resulted, at its best, in 79.4 ± 0.8% and total AR, as shown in Fig. 5. This demonstrates that the first zone (alcohols) of Fig. 6 would equal or even enhance the industrial yields. Therefore, these are promising results since these alcohols are also recommended solvents by scientific criteria.

4.2. Solvent to crude ratio discussion

Different results for each solvent were observed when the deasphalting model was simulated. Fig. 7 shows the y_E (a)), AR (b)) and S_H (c)) for six solvents. Note that the selectivity axis is logarithmic.

Generally, when increasing the R–S/C, the y_E rises and the AR reduces. The SH reduces in most cases, except for methanol and ethylene glycol. According to these tendencies, higher R–S/C implies a carryover of all the SCO families to the DAO, including a higher amount of the heavy fraction, and thus, lower quality of the DAO. Therefore, the R–S/C selected will depend on the yield and asphaltenes and sulfur and metals content required for the DAO. Since the DAO will be sent to the refining process, we consider that higher yields (y_E) are preferred, whenever AR is satisfactory, e.g., if the DAO is going to be sent to catalytic conversion units, the quality required for the DAO is higher and then, a higher AR is needed despite the lower y_E.

4.3. Temperature effect

Deasphalting is a medium temperature process, which proceeds between 40 and 150 °C depending on the solvent (Speight, 2020). The extraction temperature has to be high enough to get the crude oil fluid

Table 5

Properties of the solvents used: boiling point (BP, °C), solvent type, and recommendation from literature (Prat et al., 2014).

| Solvent	BP (°C)	Solvent type	Recommendation	BP reference
DMF (N,N-dimethyl-formamide)	152.95 ± 1.0	Aprotic polar	Hazardous	Joshi et al. (1990)
DMA (N,N-dimethylacetamide)	165.05	Aprotic polar	Hazardous	(Weast et al., 1989)
NMP (1-methyl-2-pyrrolidinone))	202.05	Aprotic polar	Hazardous	(Weast et al., 1989)
Sulfolane	287.85	Aprotic polar	Recommended	Lee (1986)
Methanol	64.65 ± 0.3	Alcohol	Recommended	Blanco and Ortega (1998)
Isopropanol	82.35 ± 0.4	Alcohol	Recommended	Hiaki et al. (1995)
Tert-butanol	82.35 ± 0.7	Alcohol	Recommended	Loras et al. (1999)
Ethylene glycol	197.35 ± 0.5	Alcohol	Recommended	(Weast et al., 1989)
Ethyl acetate	77.05 ± 0.2	Ester	Recommended	Blanco and Ortega (1998)
n-Propyl acetate	101.55 ± 0.8	Ester	Recommended	(Weast et al., 1989)
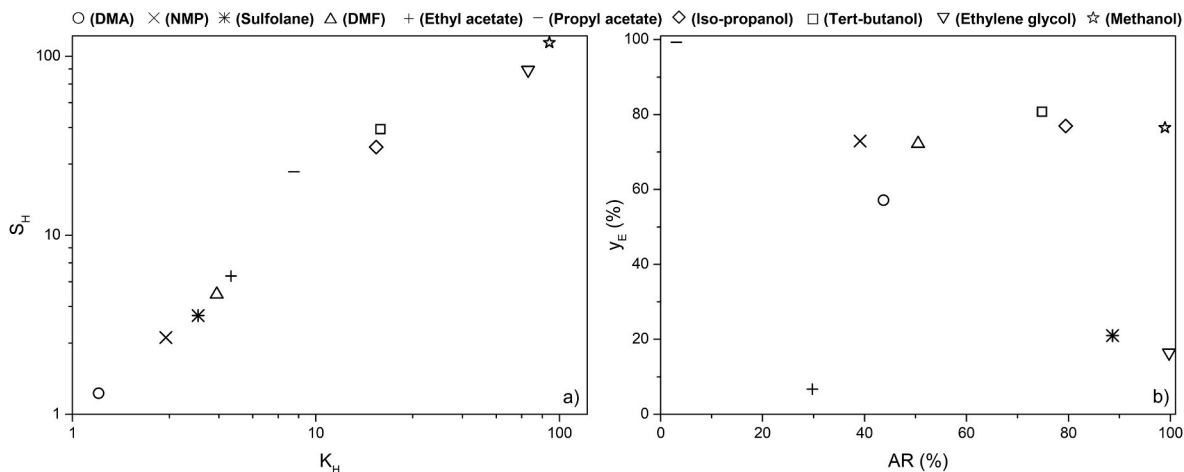
Fig. 6. Results for each solvent used. a) partition coefficient (K_H) vs. selectivity (S_H); b) asphaltene reduction (AR) vs. extraction yield (y_E).
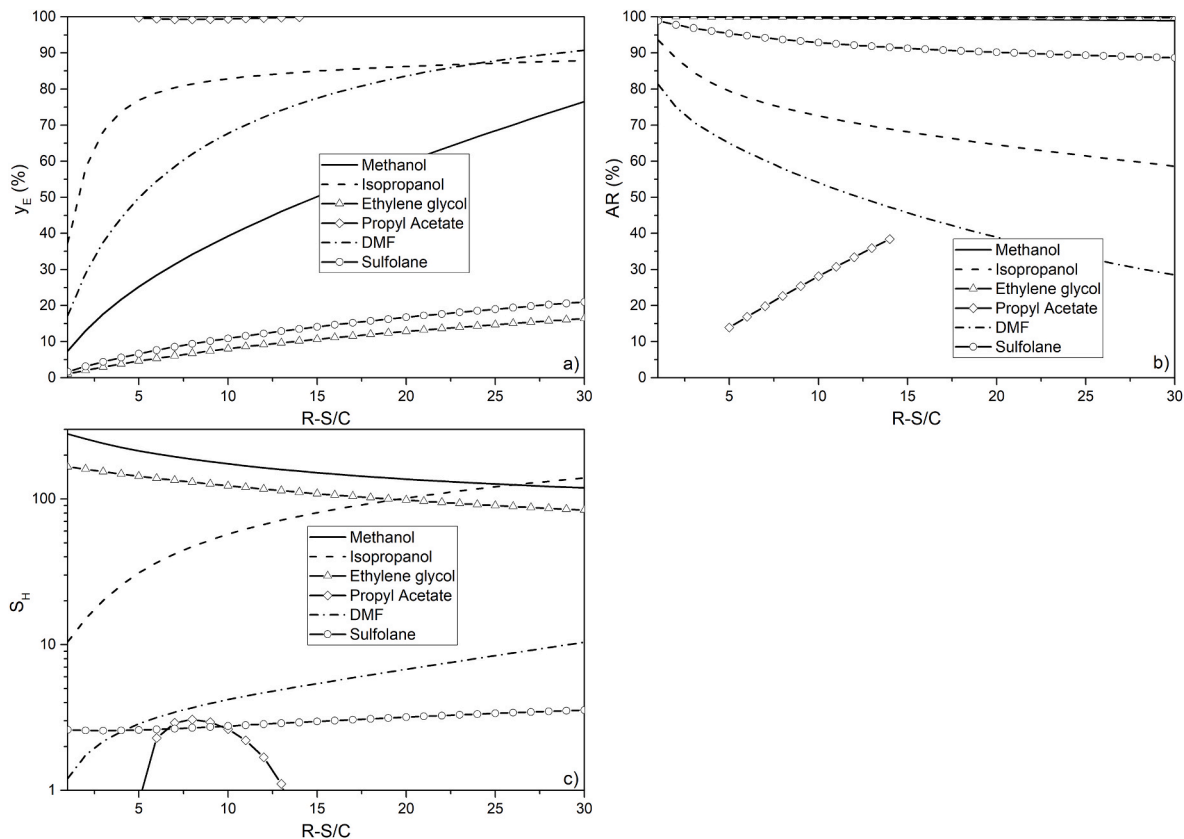

Fig. 7. Extraction yield (y_E), Asphaltene reduction (AR), and selectivity (S_H) in the function of the solvent to crude ratio (R–S/C) for six solvents.

and to obtain a satisfactory yield but without overpassing the thermal degradation temperature of the crude. The use of alternative solvents could widen the range of available temperatures while yielding sufficiently. Fig. 8 shows the comparison of S_H, K_H, y_E, and AR obtained for the best results of each solvent between both temperatures (20 & 50 °C). The analysis of the different temperatures showed multiple behaviors of the solvents. The increase of the temperature in alcohols mostly showed an improvement of the deasphalting, with an average rise of 24% of the selectivities, but it led to a slight decline of the AR due to a carryover effect in the heavy fraction. The methanol y_E decreased a 45%. The iso-propanol was an exception with an extraction enhancement without side effects.

The aprotic polar solvents presented different results. The DMF showed an improvement of the AR of 26% with higher temperatures and a decrease of the S_H of 28%. Moreover, when the R–S/C is raised from 14 to 30, the y_E descends a 26%. The sulfolane obtained worse separation, lowering the S_H a 20% and the y_E an 11%. The NMP did not show remarkable changes in its results. The DMA showed a major LLE and the S_H raised an 18% and the y_E augmented a 33%, but with a worsening of the AR, descending a 37%. Finally, the ethyl acetate did not produce LLE at 50 °C. The propyl acetate enhanced its AR to 13%, but still, this result is very poor.

In conclusion, the increase in temperature produced slightly better results in the AR, S_H, and K_H with an average increase of 37%, 8%, and 9% respectively. However, an average negative effect was observed in the y_E in most cases of 7%. The temperature effect did not show an important influence on the process and the poor improvement of the results may not justify a higher temperature and its corresponding costs.

5. Conclusions

In this work, the necessity of a deasphalting model that can be applied and modified for different feedstocks and conditions has been satisfied. The deasphalting model is formed by the combination of a discrete pseudo-component-based crude oil model and a deasphalting unit with an approach of an LLE with the predictive group contribution thermodynamic model mod. UNIFAC (Dortmund) implemented in Aspen Plus®. The validation of the crude oil and deasphalting models has been appropriately performed in two ways with different experimental and literature data, and it showed its good reliability. The combination of both models (synthetic crude oil and deasphalting unit) allowed modeling the elimination of the asphaltenes fraction from crude oil by phase equilibrium effortlessly.

The model described in this work allows screening new solvents and potential mixtures could be proposed. We found that solvent screening using partition coefficients and selectivity as a criterion is not useful to obtain the best asphaltenes elimination. However, extraction yield and asphaltenes reduction are more accurate variables to optimize the selection and analysis. Among all the solvents used, the alcohols appear as an interesting alternative to the conventional solvents, showing high deasphalted oil flows besides large asphaltenes reduction, whose results were corroborated by experimental work. In most solvents, the higher solvent to crude ratio implied a higher extraction yield of the deasphalted oil, but its quality is reduced due to an increase in the asphaltenic content. The temperature did not affect remarkably in the results, concluding that its increase does not improve notably the deasphalting.
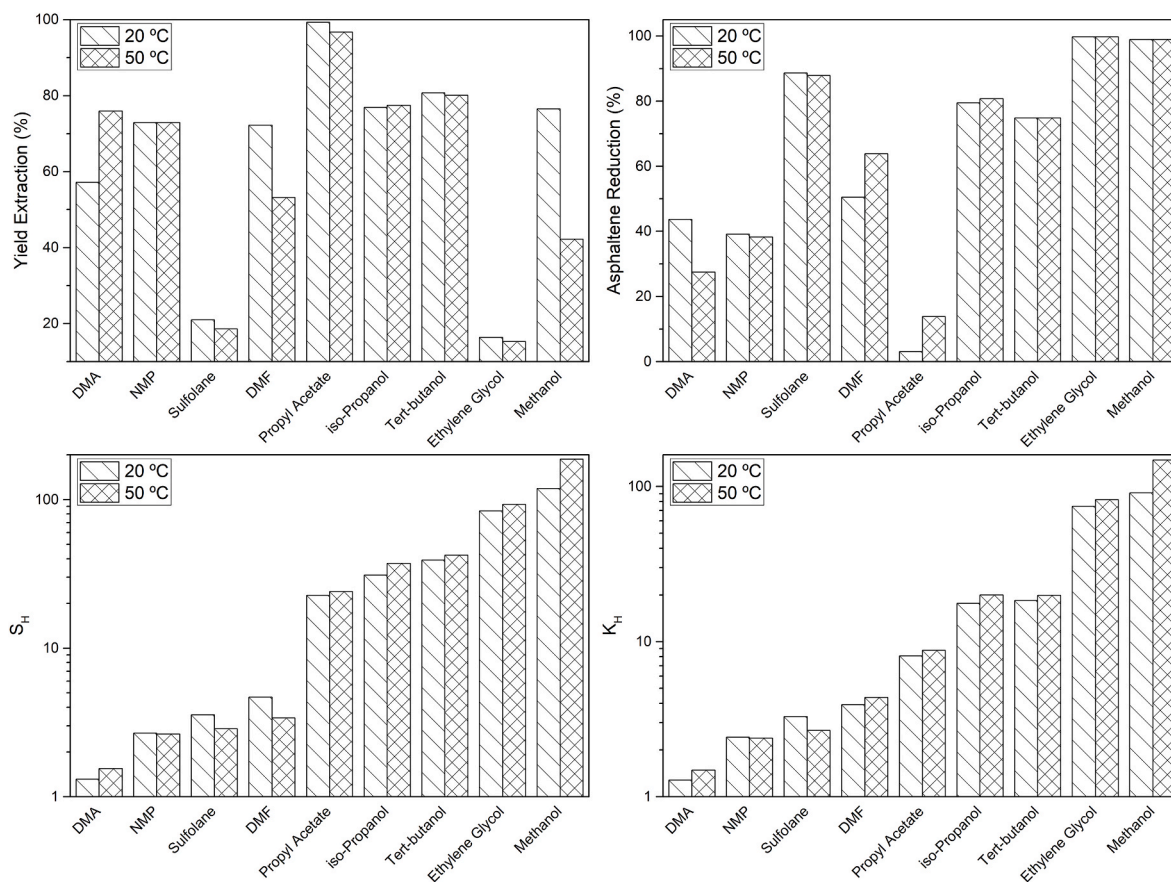

Fig. 8. Comparison between extraction temperatures of the selectivity, partition coefficient and extraction yield (y_E), asphaltene reduction (AR), selectivity (S_H), and partition coefficient (K_H).

Credit author statement

Igor de las Heras López: Conceptualization, Methodology, Validation, Investigation, Formal analysis, Data curation, Writing – Original Draft, Writing – review and editing; **Javier Dufour Andía**: Formal analysis, Writing – review and editing, Visualization, Supervision; **Baudilio Coto García**: Conceptualization, Validation, Formal analysis, Writing – review and editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.petrol.2021.109615.

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