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Integration of Solvent Extraction and Noncatalytic Esterification for the Treatment of Acidic Feedstocks

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ABSTRACT: The possibility of directly feeding the extract of a liquid−liquid extraction unit to a chemical reactor is analyzed. An example of extraction and noncatalytic esterification of naphthenic acids from acid petroleum crudes is used. Methanol is used both as a solvent and as a reactant. Separate tests of extraction and reaction are performed, and the performance of an integrated process is deduced by computer simulation. Thermodynamic and kinetic parameters for the extraction of naphthenic acids from an acid crude were determined. A partition coefficient of $m = 0.66$ at 60 °C between the alcoholic and petroleum phases was found. Three successive batch extractions with a 1:1 v/v ratio reduced the acidity from 4.3 to about 1.1 $mg_{KOH}\ g^{-1}$. Naphthenic acid concentrates were reacted with supercritical methanol in a batch reactor at high temperatures (280 °C), yielding naphthenic esters. Reaction of 1−2 h with methanol-to-oil molar ratios of 3−6 yielded 92−96% conversion because of a relatively low value of the equilibrium constant. Total conversion could, however, be achieved with the highly diluted extracts. Simulations were run using three countercurrent mixer−settlers and a noncatalytic reactor. The results indicated that extraction/supercritical esterification is a convenient pretreatment step of acidic feedstocks because of its simplicity, the good quality of the deacidified feedstock (acidity <0.5 $mg_{KOH}\ g^{-1}$), the total removal of the acids, and the good properties of the ester product as a fuel additive. Characterization of the methyl naphthenate product showed that it had a lower viscosity than the crude or the naphthenic acids; a high flash point; and total miscibility in gasoline, kerosene, and diesel. These and other properties showed that it could be sent to the diesel or fuel oil pools.

1. INTRODUCTION

Liquid−liquid extraction (LLE) is an important operation unit in chemical engineering. Distillation, the workhorse of separation processes, is based on boiling point differences. LLE is, however, based on the different relative solubilities of the solute in the two immiscible, or partially miscible, feed and solvent liquid streams. Extraction is used as a replacement for distillation in cases in which the latter is not cost-effective or not technically possible.[1] This is the case in the separation of azeotropic mixtures, the separation of mixtures with components of similar volatility, or the distillation of mixtures containing heat-sensitive materials that decompose at the high temperatures of distillation.[1,2]

Liquid−liquid extraction occurs between two liquid phases. One is the feed that consists of a solute and a carrier. The other phase is the solvent. Extraction comprises the transfer of the solute from the feed to the solvent. During extraction, the feed becomes progressively depleted of solute, and at the end, it becomes a raffinate, while the solvent turns into an extract. Solvent and feed must be mutually immiscible or slightly miscible, so that a dispersion can be formed in which one liquid is dispersed as droplets in the other.[1−3]

In this work, we analyze the possibility of coupling an extraction unit to a reaction unit by sending the extract directly to a chemical reactor. This combination seems appealing in two possible cases: (i) when the solvent of extraction is also a needed and suitable reagent for the reaction unit and can be advantageously used in the same chemical plant, thus reducing the number of process steps, and (ii) when the solvent of extraction does not act as a reagent but it is a suitable solvent for carrying out a reaction on the solute with good activity and selectivity to the desired product. These two requirements add to other requirements for choosing a suitable solvent for extraction. These have been extensively reviewed in the literature[4−6] and can be summarized as follows: (a) a high solubility for the solute and low solubility for the feed; (b) a density difference with the feed, higher than 0.15 $g\ cm^{-3}$; (c) a medium value of surface tension (5−30 $dyne\ cm^{-1}$); (d) a high resistance to thermal degradation if solvent regeneration by evaporation is used; and (e) a low viscosity for ease of handling.

Noncatalytic esterification is a brute-force method making use of the nucleophilic reactive properties of supercritical alcohols. From a process point of view, it has the advantage that it is scalable to any scale of production and is easily implemented. Major drawbacks in comparison to catalytic esterification are the high temperature and pressure levels involved and the need for efficient heat-recovery schemes.[7−10] In this report, the esters obtained in the supercritical reactor

are characterized to check their quality as a fuel according to known standards.

A process was studied in which an acid petroleum crude with a high value of total acid number (TAN) is extracted with methanol to make the resulting raffinate suitable for refining without the addition of corrosion inhibitors in standard refineries that have no special metallurgy in reboilers or hot sections of process units. The desired resulting TAN value of the raffinate should thus be lower than 0.5 mg$_{KOH}$ g^{-1}. The extraction of naphthenic acids (NA) with alcohols has been extensively studied, especially by refining companies, for decreasing the total acid number (TAN). In these reports, both monohydric and polyhydric alcohols have been used, but the applications have made extensive use of basic reagents in the solvent, especially ammonia.[11,12] Scarce reports are found, for example, for extraction of crudes with single methanol.[13] Esterification, either subcritical-catalytic or noncatalytic-super-critical,[14−20] has also been used to reduce the TAN of crudes. However, the reaction has always been tried on the entire crude, thus leading to two unattractive results: (i) the ester product cannot be further separated downstream the reactor to be used for other purposes and (ii) the esters are processed downstream in the refinery, thus being dehydroxygenated in the hydrotreatment reactors with a significant penalty for hydrogen consumption.

A cost-effective method for reducing the TAN of acidic petroleum crudes is indeed highly attractive. Acidic crudes are "opportunity" crudes with a reduced market price, usually 80% of the price of conventional crude oil. As the cost of crude accounts for about 90−95% of the total running costs of refineries, if the acid crude could be smoothly processed, it would lead to substantial savings.[21]

In the example studied here, naphthenic acids (NAs) are first extracted and then reacted to methyl naphthenates (MeN). This spares most of the crude from the thermal stress of the reaction and minimizes the chemical reactor volume. It also permits recovering naphthenic esters separately so that they can be used as final products. The properties of these esters are studied here to determine their useful features. Properties assessed are sulfur content, viscosity, boiling range, flash point, and miscibility.

2. MATERIALS AND METHODS

The general procedure was as follows: (i) liquid−liquid equilibrium data was obtained for the solvent−feed−solute system in the form of partition coefficients; (ii) kinetic parameters for extraction in a stirred tank extractor were obtained in the form of the global average mass transfer coefficient, aK_L (in min^{-1}), which is the product of a, the interfacial area per unit volume of the extractor, and K_L, the solvent-side mass transfer coefficient for liquid−liquid extraction; (iii) reaction thermodynamics and kinetics data for the esterification of NA with supercritical methanol were obtained under varying reaction conditions from batch tests and from literature reports; (vi) simulations were run for continuous units, varying process conditions; and (vi) properties of the obtained esters were determined by standard tests.

2.1. Materials. The solvent used, methanol, was supplied by Biopack (Buenos Aires, Argentina). The chemical purity was higher than 99%. All compounds were used without further purification. Acidic crudes were supplied by Y-TEC and corresponded to crudes from El Corcobo reservoir, south of Mendoza province (Argentina). Other solvents and reactants were supplied by different vendors: isopropanol (Ciccarelli, 99.5%), toluene (Merck, 99.9%), potassium hydroxide (Merck, 99.95%), and distilled water.

2.2. Liquid Extraction Equilibrium and Kinetics. The feed−solute−solvent system was petroleum−NA−methanol. The NAs were distributed between the oil phase and the alcohol phase (methanol rich). Experimental data was obtained in a stirred tank reactor. This was an AISI 304 stainless steel vessel with 100 mL total volume, 40 mm diameter, and 80 mm length. The vessel was heated in a tubular furnace, and the temperature was controlled with a Novus N1100 controller and a thermocouple. The amounts of each component for preparing the solutions were determined by weighing in an analytical balance (Shimadzu AUW220D dual range balance, 0.0001 g precision). The mixtures were vigorously stirred for 4 h and then left to rest for at least 12 h. This led to the formation of two phases, a dark one (petroleum) and another clear one (alcohol), with a well-defined interface. Each phase was sampled for analysis with the aid of a pipette. The acidity of the samples was determined by potentiometric titration (AOCS Method Ca 5a-40) with a micro-burette. The amount of methanol in the oil phase was determined by weighing the liquid before and after evaporating the solution (80 °C, 300 mm Hg vacuum). The amount of oil in the methanol phase was determined from a mass balance of the previous components. The analysis was repeated at least three times, and the average of these readings was taken as the liquid phase composition.

For measuring the extraction kinetics, the technique of Schindler and Treybal[22] was first tried but the petroleum crude was difficult to pump with the available peristaltic pumps. The stirred tank of the equilibrium tests was therefore used for measuring the evolution of the acidity as a function of time, and then the coefficient of mass transfer was fitted from these data and an appropriate model.

2.3. Settling Tests. Tests of settling rates were performed for the petroleum−methanol system by vigorously stirring mixtures of varying solvent-to-oil ratios and then allowing them to rest at a controlled constant temperature. The time was recorded when two distinctive phases were formed and no oil phase remained in suspension in the upper phase.

2.4. Reaction Tests. They were performed using a discontinuous autoclave reactor of small volume, as previously described.[8−10] Extracts obtained by extraction of the petroleum crude with methanol were used for the reaction. In a typical experiment, the extract was put in the reactor, filling it almost completely. Then, it was purged with nitrogen to remove the trapped air. Then, it was heated to the reaction temperature by means of a tubular furnace. The total pressure corresponded to the autogenerated pressure of the reacting mixture. The reaction temperature chosen was 280−320 °C (the critical temperature of methanol is 239.3 °C) to ensure that the supercritical state of methanol was achieved.

2.5. Product Characterization. Several properties of the product of the reaction, methyl naphthenate, were measured. Viscosity was measured either with a Brookfield RVT viscometer or with glass Cannon−Fenske viscometers following the standard ASTM D445 and using a thermostated oil bath for constant temperature measurements. The acidity of the samples was determined by potentiometric titration (AOCS Method Ca 5a-40) with a microburette. The sulfur content was determined by organic elemental analysis in a LECO analyzer model 744. The boiling range was determined by means of simulated distillation runs in a gas chromatograph. In general, the ASTM D2887 standard was followed. The equipment used was a Shimadzu 2014 gas chromatograph and a Restek MXT-1 metal megabore column. The flashpoint of the methyl naphthenates was measured using the open-cup test method.

3. RESULTS AND DISCUSSION

3.1. Theoretical Analysis. A scheme of the proposed combination of operations to be used in the final implementation is included in Figure 1. The liquid−liquid extraction unit can be a countercurrent contact column or a series of mixer−settler units. Mixer−settlers are preferred because petroleum is difficult to disperse in small droplets. The supercritical reactor is a heated tube with a high length-to-diameter ratio to avoid backmixing problems arising from the
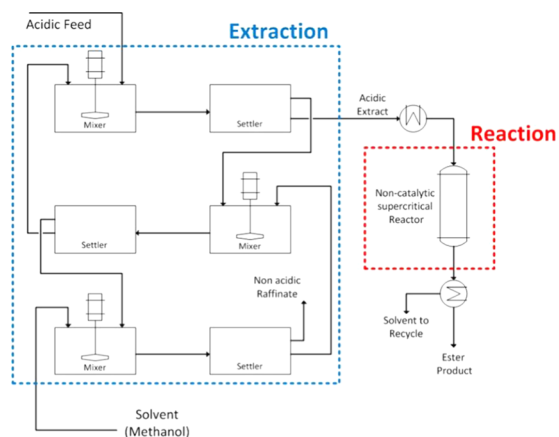
Figure 1. Scheme of the proposed process matching a liquid–liquid extraction cascade with a noncatalytic transesterification reactor.

high diffusivity of supercritical methanol.[23] At the exit of the reactor, the mixture of methyl naphthenates could be recovered by distilling off the methanol.

This process can be modeled by writing a set of ordinary differential equations as a function of time (for the tanks) or axial distance and time (for the tubular reactor). For an equilibrium two-phase mixture of alcohol and oil, x and y can be supposed to be related by means of Nernst's law, eq 1, if the two phases are immiscible and the concentration of the solute is low.[24] N is the number of moles of impurity (NA) transferred from the oil to the alcohol phase, per unit volume of tank extractor (in mol s^{-1}). a is the interfacial area per unit volume of the extractor (in m^2 L^{-3}). ϕ is the hold-up of the disperse, oil phase (adimensional). y is the impurity concentration in the alcohol phase (in mol L^{-1}). x is the impurity concentration in the oil phase (in mol L^{-1}). K_{MeOH} is the global mass transfer coefficient for liquid–liquid extraction (K_L), on the side of the solvent (in m s^{-1}). V is the tank volume (in L); F_v is the volumetric flow rate of oil or methanol (in L s^{-1}). Equations 2–4 are valid for any of the three tanks. The subscript "in" indicates interface values.

$$y_{eq} = m x_{eq} \tag{1}$$

$$N = a K_{MeOH}(mx - y) \tag{2}$$

$$\frac{dy}{dt} = \frac{N}{1-\varnothing} + \frac{F_v^{MeOH}}{V(1-\varnothing)}(y_{in} - y) \tag{3}$$

$$\frac{dx}{dt} = -\frac{N}{\varnothing} + \frac{F_v^{oil}}{V\varnothing}(x_{in} - x) \tag{4}$$

$$\frac{\partial y}{\partial t} = D_a \frac{\partial^2 y}{\partial z^2} - v\frac{\partial y}{\partial z} - r \tag{5}$$

Equation 5 is the equation for the variation of y inside the tubular reactor when taking axial dispersion and reaction into account. It has been suggested by Busto et al.[23] that tubular reactors performing transesterification reactions with supercritical alcohols should include this term because of the high diffusivity of supercritical alcohols. It will be disregarded here, assuming that a high length-to-diameter reactor ratio is used. v is the spatial velocity of the fluid phase (in m s^{-1}). r is the chemical reaction rate (in mol L^{-1} s^{-1}). Note that $C_{NA} = y$ at the reactor entrance, i.e., the concentration of NA in the extract at the outlet of the extraction unit is the NA concentration of the feed to the reactor.

Considering the more general bimolecular model (eq 6), it must be taken into consideration that esterification of organic acids with alcohols is a reversible reaction with a relatively small Gibbs free energy of reaction, i.e., with small values of the equilibrium constant. Kinetic parameters should follow the Arrhenius law and should be related by thermodynamic equilibrium (eqs 7–9).

$$NA + MeOH \underset{k'}{\overset{k}{\leftrightarrow}} H_2O + MeN \tag{6}$$
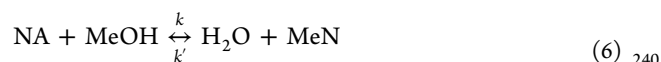
$$k = A\,e^{-E_a/(RT)} \quad \text{(forward reaction)} \tag{7}$$

$$k' = A'e^{-E_{a'}/(RT)} \quad \text{(inverse reaction)} \tag{8}$$

$$K_{eq} = k/k' \quad \text{(equilibrium constant)} \tag{9}$$

$$r = k\,C_{MeOH}C_{NA} - \frac{k}{K_{eq}}C_W C_{MeN}$$

$$\text{(bimolecular reaction, 2nd order)} \tag{10}$$

$$k^* = k\,C_{MeOH} \quad \text{(pseudo first order constant)} \tag{11}$$

$$r^* = k^* C_{NA} \quad \text{(first order reaction kinetics)} \tag{12}$$

For the reaction of naphthenic acids in high-temperature alcohols, first- and second-order models have been posed (see Table 1). Also, reactions with subcritical and supercritical methanol have been reported. In the case of first-order models with experimental data with high methanol-to-oil ratios (e.g., Zafar et al.[14]), it can be considered that this is a reduced form of the model of eq 6 in which the methanol concentration has been lumped into the kinetic constant because it is practically constant under those reaction conditions (see eqs 11 and 12).

The relatively low value of the equilibrium constant for esterification has prompted some authors to consider both the forward and inverse reactions when studying the kinetics of nondiluted systems. This is frequently the case for the noncatalytic esterification of free fatty acids with methanol[25,26] but rare in the case of esterification of naphthenic acids. The thermodynamic limitations on conversion caused by the small value of K_{eq} become worse at higher temperatures because

Table 1. Reported Data on the Kinetics of the Noncatalytic Esterification of NAs with Methanol

refs	model	A factor	E_a (J mol^{-1})	system conditions
14	$r = kC_{NA}$	1.56 s^{-1}	24 170	mixture of NAs, 300–350 °C, highly diluted NAs, supercritical
15	$r = kC_{NA}^2$	127 L mol^{-1} s^{-1}	54 150	mixture of NAs, 150–210 °C, 2 MPa, subcritical
16	$r = kC_{NA}$	174 s^{-1}	58 420	cyclopentanoic acid, 220 °C, 3 MPa, subcritical
17	$r = kC_{NA}^2$	45 167 L mol^{-1} s^{-1}	7227	acid petroleum, TAN = 7.33, 150–250 °C, mostly subcritical

$^a C_{NA}$: concentration of naphthenic acids in methanol ($C_{NA} = y$), mol L^{-1}. C_M: concentration of methanol, C_W: concentration of water.

esterifications are mildly exothermal. The literature is also abundant on attempts of displacing the equilibrium. Lucena et al.[27] found low conversion values at mild temperatures and resorted to water elimination in an adsorption apparatus to shift the equilibrium to product formation. Metre and Nath[28] found values of K_{eq} of 0.2–1.7 at 40–60 °C when reacting palm fatty acids with methanol in the presence of phosphoric acid. Sharma et al.[29] reported a value of 0.3–0.5 for the equilibrium constant of esterification (K_{eq}) of tuna free fatty acid with methanol at 25–35 °C, and the equilibrium was not shifted to the formation of products at higher temperatures. Anikeev et al.[30] estimated approximate values of K_{eq} for the esterification of palmitic acid with methanol and reported that the equilibrium constant decreased by about 10^2 from 80 to 300 °C.

For esterification with methanol without a catalyst, the results indicate that the reaction is faster when using supercritical methanol. In this sense, the reactivity pattern of esterification of naphthenic acids is similar to that observed for the transesterification of fatty acids (see Figure 2). Two regions of different reactivity can be detected, with a transition region at 240–260 °C.
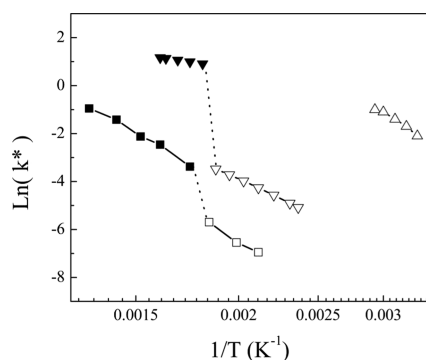

Figure 2. Values of the (pseudo) first-order kinetic constant for the forward reaction of esterification with methanol. Hollow symbols show data of reaction with subcritical methanol; full symbols show supercritical methanol. (■,□) Noncatalytic transesterification of plant oil.[31] (▼) Noncatalytic-supercritical esterification of naphthenic acids.[14] (∇) Noncatalytic subcritical esterification of naphthenic acids.[17] (△) Catalytic subcritical transesterification of soy oil with dissolved NaOH.[32]

The matter of the equilibrium constant is especially important in the case of esters to be used as fuels or additive for fuels. The fuel standards usually have very small limits for free acids because of the problems associated with the corrosion of metals. In this sense, total conversion of the acids should be achieved.

In the case of the esterification of naphthenic acids, no attempt has been made to fit a kinetic model including the reverse reaction. In this sense, the adoption of second-order models[15,17] could point to an "artifact" in which the reduction of the total reaction rate at high conversion values is misinterpreted as a consequence of the high order of reaction when really it is due to a thermodynamic limitation.

A bimolecular first-order kinetic model will be used, with two parameters: the forward rate constant, k, and the equilibrium constant, K_{eq} (see eq 10). C_{MeN} is the concentration of methyl naphthenate. The value of the kinetic constant for the forward reaction will be taken from the kinetic

data of Zafar et al.[14] for the supercritical range and the data of Quiroga-Becerra et al.[17] for the subcritical range. These data show a pattern of reactivity similar to the transesterification of plant oils with methanol (see Figure 2). The constant for esterification is higher than that of transesterification, but both have a discontinuity when entering the supercritical range, the supercritical kinetic constant being higher than the subcritical one.

3.2. Experimental Equilibrium Constant. Values of the equilibrium constant at 280 °C were measured by running discontinuous reaction tests at different methanol-to-oil ratios and long times and measuring the final conversion (X). Then, the equilibrium constant was calculated according to eq 13.

$$K_{eq} = \frac{X^2}{(1-X)(\beta - X)} \tag{13}$$

The average value for K_{eq} at 280 °C is 4.08 considering the longer reaction times (Table 2). Taking into account the

Table 2. Values of Conversion at 280 °C for Different Values of the Methanol-to-NA Molar Ratio (β) and the Reaction Time, Θ; β (mol mol^{-1})[a]

T (°C)	β	Θ (h)	X (%)	K_{eq}
280	6	0.5	91.6	1.96
280	6	1	96.3	4.98
280	6	2	96.5	5.28
280	3	1	93.6	6.63
280	6	1	95.0	3.57
280	20	1	94.4	0.84
300	6	1	94.9	3.50
320	6	1	93.3	2.56

[a]Samples prepared by diluting commercial NAs in methanol.

points at different temperatures, the heat of reaction is 12.9 J mol^{-1}. The results confirm the known fact that esterification reactions have a low equilibrium constant and low exothermal heat of reaction.

The experimental point of $\beta = 20$ yielded the lowest calculated K_{eq} value, but this outlier was disregarded because of probable experimental problems.

3.3. Experimental Partition Coefficient m and Mass Transfer Coefficient aK_L. For the system petroleum−NA− methanol, values of m were obtained from sets of data of x and y for different extraction tests at different temperatures (see Figure 3). m was calculated as the ratio of the concentration of acid in the alcohol phase (free of oil) to the concentration of free fatty acid (FFA) in the oil (free of methanol). At 60 °C, the value of the partition coefficient is $m = 0.66$ (mol L^{-1})/ (mol L^{-1}).

During an extraction test, the concentration in the oil phase decreased as a function of time until equilibrium was reached. This happened at about 2 h (see Figure 4). This is a medium process time, and it is due to a relatively low value of the aK_L for this system. Values of the aK_L can be obtained for the stirred tank using the data of NA concentration as a function of time. Solving the model of eqs 1−4 with the corresponding m value from the isotherm, aK_L can be regressed with a least-squares program. This procedure yields a value of $aK_L = 0.19$ s^{-1}, for a stirring rate of 1365 rpm, 60 °C, and a methanol-to-oil ratio of 1:1 v/v (equivalent to hold-up of 0.5). The value corresponds to a medium aK_L value of a stirred tank, according
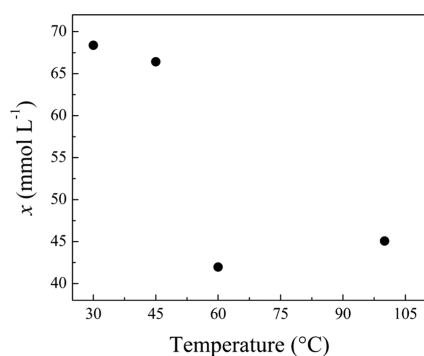
Figure 3. Equilibrium concentration of NAs in the oil phase (x) after a discontinuous extraction test, as a function of temperature. 1:1 methanol-to-oil volume ratio, 60 °C, initial TAN = 4.37 mg$_{KOH}$ g^{-1} (68.38 mmol $_{KOH}$ L^{-1}).
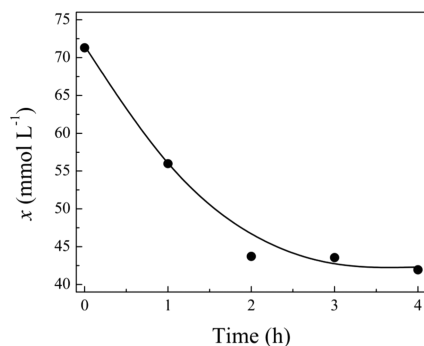

Figure 4. Concentration of NAs in the oil phase (x) as a function of time during a batch extraction test at 60 °C. Initial TAN = 4.37 mg$_{KOH}$ g^{-1}.

348 to the report of Schindler et al.[22] For different values of the
349 methanol-to-oil ratio, the aK_L can be approximately linearly
350 extrapolated by considering that the aK_L coefficient for a
351 stirred tank is proportional to ϕ, the disperse-phase hold-up.[33]
352 Operation of a mixer−settler cascade demands that the
353 operation of the mixers and the settlers temperature be the
354 same. In the case of the mixer, the higher solubility of NAs in
355 methanol at higher temperatures is also accompanied by a
356 higher solubility of the oil in methanol. Hence, there must be a
357 balance when choosing the right temperature of operation
358 because the relative purity of the extract or the yield of raffinate
359 can be an issue. In the case of the decanter, however, the
360 higher the temperature, the better, because it produces a
361 decrease in both viscosity and surface tension, and hence a
362 decrease in the settling time. However, the same concerns
363 apply to the increase of mutual solubility between methanol
364 and oil.
365 Some tests of settling time were performed. Petroleum/
366 methanol mixtures with 1:1, 1:3, and 1:10 v/v ratios were used.
367 The system was stirred for 10 min, and then it was allowed to
368 rest. The time was registered when two distinct clear phases
369 with a defined interphase were formed. The results indicated
370 that there was a time t^* at which two phases were rapidly
371 formed, though complete settling was not achieved, and a final
372 time t^{**} at which settling was finished. At 25 °C, t^* was less
373 than 1 min at 25 °C for any dilution used but t^{**} was 4 h. At
374 60 °C, t^* was 10 min and t^{**} was 80 min (1:10 vol ratio), 130
375 min (1:3 vol ratio), or 200 min (1:1 vol ratio).
376 The first rapid separation at t^* is due to the big difference of
377 density between the two phases. However, a clear final

378 separation takes longer. In this sense, the settlers are the slow
379 unit of the process, needing more residence time than the
380 extraction tanks.
381 A set of three consecutive steps of extraction with fresh
382 methanol was performed with a methanol-to-oil volume ratio
383 of 1:1 to check the possibilities of the method for reducing the
384 TAN. Two hour extraction and 2 h settling times were used.
385 The TAN of the last raffinate was 1.1 mg$_{KOH}$ g^{-1}. It is obvious
386 that higher methanol-to-oil ratios are needed to achieve a value
387 of TAN of 0.5 or lower.
388 **3.4. Characterization of the Feedstock, Extract, and**
Methyl Naphthenate. Simulated distillation curves are
389 plotted in Figure 5. The mass-averaged boiling point of the
390 mixtures was 286 °C for the commercial sample and 296 °C
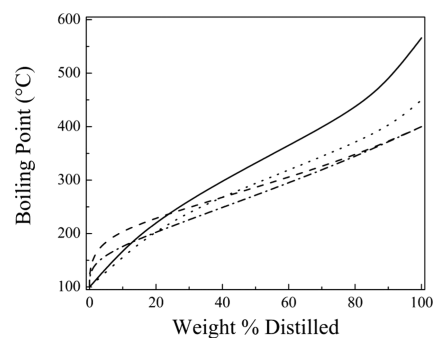391 for the extract from the crude.
392

Figure 5. SimDis results. Solid line: crude sample. Dashed line: commercial NA sample. Dotted line: extracted NA. Dashed−dotted line: methyl naphthenate ester product (MeN, reaction for 1 h at 280 °C, with $\beta = 6$).

393 Mass percentages of NA in (Table 3) were calculated from
394 mass balances and acidity measurements.

Table 3. Comparison of Properties[a]

property	crude	commercial NA	extracted NA	MeN
mass percentage of NA, %	1.8	95	93	6.1
acidity, mg KOH per gram	4.99	350	310	17
density, g cm^{-3}	0.905	0.93	0.91	0.92
viscosity, cSt, 45 °C	262	16.3	21.4	3.2
sulfur content, ppm	9100		5.6	
boiling range, SimDis 2887 wt %				
100−150 °C	7.1	0.0	8.8	0.0
150−200 °C	15.4	5.9	18.6	18.5
200−250 °C	26.7	30.0	32.7	40.5
250−300 °C	40.4	57.6	52.3	62.3
300−350 °C	55.4	81.8	72.5	82.4
350−400 °C	70.6	100.0	90.6	100.0
400−450 °C	83.6		100	
450−500 °C	91.8			
500−566 °C	100.0			
water solubility, mass %				0.17
flashpoint, °C				124

[a]Crude: unrefined petroleum sample. Commercial NA: mixture of concentrated NAs. Extracted NA: from the original crude, with three consecutive extractions, 1:1 v/v. MeN: methyl naphthenate ester product (reaction of commercial NA with methanol for 1 h at 280 °C, $\beta = 6$).

E

The residual acidity of the MeN samples is a consequence of the equilibrium limitations and the relatively mild methanol-to-oil ratio used in the reaction tests. The residual acidity could be eliminated by running two reactions with intermediate removal of water or by increasing the methanol-to-oil ratio of a single reaction.

The commercial NAs had practically no sulfur. This must be related to the origin of petroleum. Petroleum molecules containing both carboxylic and sulfur groups are rare, but they have indeed been detected in some petroleum crudes. For example, West et al.[34] found diaromatic molecules containing both S and carboxyl groups and Wu et al.[35] found that NA samples from oil sands could have 1−5% sulfur.

The petroleum crude and methanol are immiscible, while the NAs are soluble in methanol. The MeN product is completely soluble in a variety of fuels and solvents. It is completely soluble in methanol, n-heptane, kerosene, gasoline, and diesel. When put in contact with a 50:50 solution of methanol/heptane, it acts as a cosolvent. A 40:40:20 mixture of methanol/heptane/MeN forms a single phase. When MeN is added to a 50:50 methanol/diesel mixture, it does not work as a cosolvent and the system continues to have two phases, an upper layer of methanol and a bottom layer of diesel. MeN is distributed among the phases, but it is preferentially dissolved by the diesel phase (Table 4).

Table 4. Properties of Some Fuel Types According to ASTM Standards[a]

property	kerosene	diesel	heating oil	MeN
sulfur, mass %, max	0.3	0.05−0.5	0.3−0.5	
API gravity at 60 °F, max		38	35	22
flashpoint, minimum, °C	38	52	38	124
boiling range				
10% recovered, °C, max	205		215	175
end point, °C, max	300	355 (95%)	288−338 (90%)	400
viscosity, cSt, max	1.9	4.1	2.4−4.1	3.2
cloud point, °C, max				−9
acid number, mg_{KOH} g^{-1}, max		0.2	0.3	

[a]Comparison with MeN.

A comparison of properties of the methyl naphthenate and some limit properties of standardized fuels is shown in Table 3. Cloud point limits are location-specific and were therefore not included. It can be seen that methyl naphthenate is a relatively low-density product, with low sulfur and low viscosity. Its properties allow it to be blended into the diesel or fuel oil pools, but the low-volatility fraction (heavy fraction) should be removed and the acidity should be adjusted. The final acidity of MeN is a function of the degree of conversion in the reactor and can be reduced to null values if the methanol-to-oil ratio is high enough.

3.5. Process Simulation. The system of Figure 1 was simulated, i.e., the combination of three mixer−settlers for extraction and one supercritical reactor. Solutions of the system of eqs 1−6 were obtained for different values of the process variables. The main variables for running the process were considered to be the solvent-to-oil ratio at the feed of the extraction cascade and the temperature of the reactor.

For the simulation, it was considered that settling tanks were big enough so that no delay occurred in this separation unit and their modeling could be spared. Total ideal separation of the phases was considered.

Figure 6 shows a plot of the purity of the treated oil, x^{raff}, in each tank and the purity of the used solvent, y^{ext}, at the outlet,
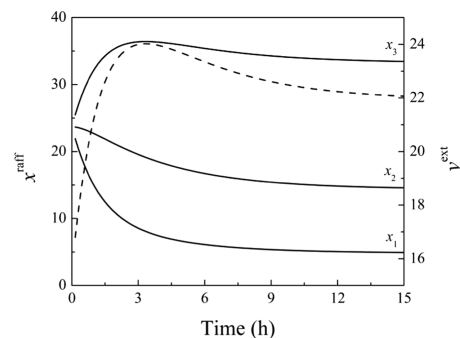

Figure 6. Continuous extraction stage, petroleum−NA−methanol system, and transient state. x^{raff} at the outlet of the first (x_1), second (x_2), and third (x_3) extraction tanks. y^{ext} (dashed line) at the outlet of the third extraction tank. 50 L extraction tanks, oil flow rate 10 L h^{-1}, methanol flow rate 30 L^{-1} (pure solvent), 60 °C. x^{feed} = 70 mmol L^{-1} (TAN = 4.37 mg_{KOH} g^{-1}), m = 0.66, and aK_L = 0.048. Final TAN = 0.305 mg KOH g_{crude}^{-1}.

as a function of time. A relatively small solvent-to-oil volume ratio, 3, was used to minimize the volume of the reactor. Minimum flow rates were considered so as to reduce the TAN of the crude to less than 0.5. With the residence time chosen (about 1 h in each tank) and the given values of aK_L and solvent-to-oil ratio, a rather long transient period is needed before the steady state is reached. The stable operation is achieved at about 15 h.

In the figure, all raffinate curves for each tank seem to begin at about 23 mmol L^{-1}, although the concentration of NA in the crude at the feed is about 70 mmol L^{-1}. This is the common value in all tanks a few minutes after stabilizing from the initial condition of $x_1 = x_2 = x_3 = x_{feed}$, $y_1 = y_2 = y_3 = y_{feed}$, at $t = 0$.

The y^{extr} values at the outlet of the mixer−settler cascade correspond to a methanol-to-acid molar ratio of about 1000. It can be seen that even for minimum solvent flow rates, the final extract to be reacted has a very high methanol-to-acid ratio. Minami et al.[36] reacted FFA and supercritical methanol with a volume ratio of methanol-to-acid of 0.9−5.4, which roughly corresponds to a 7−42 molar ratio. Quiroga-Becerra et al.[17] reacted acid crudes with methanol with a methanol-to-acid molar ratio of 20. Goto et al. used dilutions of about 20−50 mol mol^{-1}.[14] On the one hand, the high dilution is beneficial for shifting the equilibrium to the formation of esters. A diluted acid feedstock is also a guarantee of a reaction without corrosion problems in the reactor walls. On the other hand, it is detrimental to the reaction rate, leading to big reactor volumes. It is also detrimental to the solvent recovery costs because very large methanol volumes must be distilled off and recycled. In this sense, unusual solvent regeneration schemes, like those proposed by Busto et al., could be used.[6,33,37]

The steady-state values of the acid content of treated feedstocks of varying initial TANs are plotted in Figure 7 as a function of the solvent-to-feed volume ratio of the extraction stage, for the cascade of three mixer−settlers depicted in Figure 1. Low values of the methanol-to-feed ratio might lead to too high values of the final TAN, making the oil phase
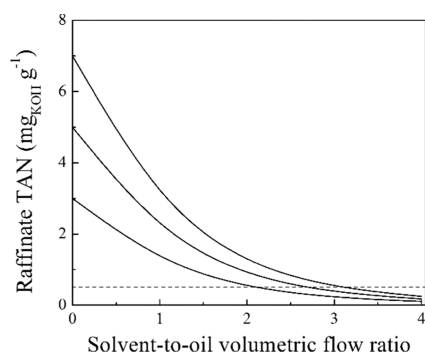
Figure 7. Steady-state values of TAN at the outlet of the extraction stage as a function of the solvent-to-oil volume ratio and the feed TAN (3, 5, and 7 mg_{KOH} g^{-1}). System of Figure 1 (three extraction stages) with properties as in Figure 6. Feed flow rate, 50 L h^{-1}. Dashed line: limit value of TAN = 0.5.

inappropriate for further refining. A horizontal dashed line represents the accepted limit of TAN = 0.5. As can be seen, values of the volume-based solvent-to-oil ratio equal to or greater than 3 are enough for petroleum crudes of TAN = 3−7 or less.

Of course, the final value of TAN is a function of not only the solvent-to-oil ratio but also the number of stages. For an initial TAN = 5, 3, countercurrent stages reduce the TAN to a final value of 0.35 with a solvent-to-oil ratio of 3, while four countercurrent stages reduce the TAN to 0.47 with a solvent-to-oil ratio of 2. The final results are similar, but each solution has different equipment and operation costs.

As can be seen in Figure 8, the conversion is rather insensitive to the reaction temperature in the supercritical
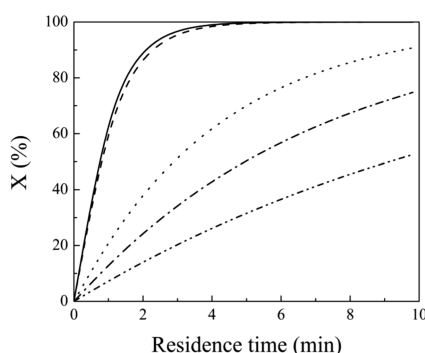

Figure 8. Steady-state total conversion of the naphthenic acids as a function of the residence time in the reactor for different reaction temperatures in the supercritical methanol range. Reaction temperature: 300 °C (solid line), 280 °C (dashed line), 240 °C (dotted line), 220 °C (dash−dotted line), and 200 °C (dash−dot−dotted line). NA concentration at the reactor inlet is 35 mmol L^{-1}. Temperatures below 250 °C are considered subcritical.

range. This is due to the high methanol-to-oil ratio. The reaction can be performed at 240 °C with the same results as 280 °C if a minimum 4 min residence time is adopted. At this time, equilibrium and total conversion are achieved. Under these conditions of total conversion, the residual acidity of the product is null and it can be blended with other fuels.

If the reaction is performed in the subcritical range (<250 °C), slower reaction rates are obtained and longer residence times are needed for total conversion.

4. CONCLUSIONS

Acid oil feedstocks can be successfully pretreated by extraction and noncatalytic esterification of the extracts. The refined crude exiting the extraction unit can be further processed without any problems due to the low level of acidity achievable. For petroleum crudes, this means that they can be smoothly refined to fuels and lubricant oils, allowing the refiners to profit from the refining of opportunity crudes.

Considering partition coefficients for NA of petroleum crudes in methanol (m = 0.66) and the mass transfer coefficients for extraction in stirred tanks, three stages of mixer−settler units with a solvent-to-oil volume ratio of 3 seem to be enough for reducing the acidity of the feedstock to acceptable levels and for further processing.

The extract phase, i.e., naphthenic acids dissolved in methanol, can be reacted in tubular noncatalytic reactors at high temperatures, with residence time values of 5−10 min, to be fully converted into an ester phase if the reaction temperature is in the supercritical range. The methyl naphthenate has low viscosity, low sulfur content, and total miscibility in diesel and other fuels, thus finding use as a contributor to the diesel or fuel oil pools.

In contrast to other published reports of the literature, the clear advantages of reacting the extract rather than the whole oil are as follows: (i) the neutral oil is spared the thermal stress at high temperatures that can lead to oil degradation; (ii) the extract according to our experiments is a clear homogeneous phase, while normal oil/methanol two-phase mixtures pose mass transfer problems for reaction; (iii) the reactor volume is reduced; and (iv) the ester phase is recovered as a separate product for later use.

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Notes

The authors declare no competing financial interest.

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