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Report on the best bench scale separation (n-, iso-paraffins etc.) or blending technology for increasing CN of upgraded naphtha

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D4.6. Report on the best bench scale separation (n-, iso-paraffins etc.) or blending technology for increasing CN of upgraded naphtha

1. INTRODUCTION

Separation and extraction of individual components from BtL-naphtha was investigated in this deliverable as an option in the case an increase in cetane number of the original BtL-naphtha is required. For this investigation a study was carried out using thirty seven (37) different naphtha samples (fully characterized in CERTH) and collected from RENEW and OPTFUELS studies and from a local refinery. Based on the results of this study three theoretical scenarios were examined for changing CN of naphtha: i) aromatics separation, ii) iso-paraffins separation and iii) removal of light components (C5, C6). The study showed that the increase of CN of BtL-naphtha is a complicated issue and its feasibility depends strongly on the CN of the raw fuel. The main conclusions were that the aromatics separation could increase CN by about 3 units. CN change by isoparaffins separation depends on the type of naphtha. For some naphthas CN could increase up to about 6 unit. The removal of light components could increase CN up to about 5 units. However, all above scenarios for CN increase have a strong negative effect on naphtha yield. Another option for changing BtL naphtha CN is the blending option with some other naphthas. From our investigation it seems that among refineries naphtha the feed to the reformer has the highest CN (of about 30) with the minimum amount of aromatics (around 10%). Naphtha coming from wax hydrocracking presents the highest CN of about 40-43 (from RENEW project studies). These naphthas are very important in case of a blending option will be adopted for changing the CN of the BtL naphtha.

Based on the above theoretical study it was decided to explore experimentally the feasibility of separation of some naphtha components from the original naphtha. The experimental results of this work are presented in the current deliverable.

Depending on its composition it can be divided into two main types: aliphatic and aromatic. These two types differ in the kind of hydrocarbons they contain. Its final composition is a direct result of both the method and the initial material used for its production. However, since naphtha itself can be used as a feedstock, it is important to be able to accurately measure its composition and separate it in its components if needed for a more efficient further processing. To this end several techniques have been developed, among which the most popular are extractive distillation, solvent extraction, adsorption of some of its components on a solid support such as SiO₂ or molecular sieves, and separation of n-paraffins by adduction with urea. A more recent approach suggests the use of ionic liquids for the separation of aromatics.

Typical solvents used for the extraction of aromatic hydrocarbons from naphtha include polyethylene glycols, sulfolane, dimethyl sulfoxide, N-methyl pyrrolidone, N-methyl morfoline and others. For a solvent to be used to this end it should present high selectivity for aromatics, high capacity, good thermal stability, capability to rapidly form separate phases at reasonable temperatures and of course it should be non-corrosive and non-reactive (Al-Sahhaf&Kapetanovic, 1996; Radwan et al., 1997; Liu et al., 2009).

Ionic liquids are organic salts that are liquid at low temperatures (<100°C) and consist of cations based on methylimidazolium, N-butylpyridinium, quaternary ammonium or phosphonium ions. The R group of the cation and the anion attached to it affect the properties of ionic liquids. Meindersma et al. (2006) have attempted to separate toluene from heptane by selectively extracting toluene using an ionic liquid as an extraction solvent. Among the liquids tested, the [methylbutylpyridinium] BF₄, was the one in which toluene demonstrated the higher partition coefficient and subsequently, the one that demonstrated the higher selectivity for toluene even at low toluene concentrations. The separation of the liquid phases can easily be done with evaporation, since ionic liquids have a negligible vapor pressure. An additional advantage of the procedure is the repeated regeneration and recycling of the ionic liquids that does not compromise their efficiency. However, ionic liquids are very expensive, and an

overall estimation of their cost effectiveness should be considered in the case of large scale applications.

Urea and thiourea adduction are simple and cost-effective methods for the separation of n-paraffins and iso-paraffins respectively, especially since they offer considerable selectivity. In its pure form, urea forms tetragonal crystals that are packed together closely enough so as to exclude the presence of other molecules. However, in the presence of an n-paraffin, in an aqueous or alcoholic solution, the urea molecules present a different trend. In particular, they tend to bond with each other forming hydrogen bonds between an oxygen atom and a nitrogen atom of the adjacent molecules. The formation of these bonds forces the molecules to turn 120° with respect to one another, thus forming helical structures. A distance of 3.7Å separates adjacent non-hydrogen bonded molecules along the axis of the spiral and the edge length of the unit cell is 4.8Å. In this molecular arrangement there exists a hexagonal channel with a diameter of 4.9Å into which the n-paraffin molecule must fit. The diameter of an n-paraffin chain is of the order of 3.8 x 4.2 Å, thus allowing the n-paraffins to fit into the channel. Thiourea complexes are formed similarly, but with a larger internal diameter, due to the larger size of the S atom. Therefore, the size of the spirals is the limiting factor for the adduct formation with the corresponding molecules, since the much larger in diameter iso-paraffin molecules, cannot fit into the urea spirals. In some cases however, a slight distortion of the urea lattice may occur and larger molecules can adduct. Apart from the diameter of the paraffin molecule, another limiting factor is the length of the hydrocarbon chain. It appears for paraffins with chains shorter than 8 carbon atoms it is difficult to form adducts with urea. (Speight, 2006; Hassan, 1994; Kim et al., 1995)

Another popular approach for the separation and recovery of n-paraffins and iso-paraffins from naphtha is the application of molecular sieves with pore size 5Å. The size of the pores is almost the same as the size of the n-paraffins molecules which therefore can be accommodated to the pores and separated from the bulk solution. The adsorption process is reversible, and the molecular sieves can be regenerated and reused. To this end, the process of pressure swing adsorption (PSA) has been proposed to be used in combination with the molecular sieves, in order to achieve enhanced separation of an n/iso-paraffin mixture (Liu et al., 2009; Sun et al., 2008; Silva&Rodriguez, 1998; Silva et al., 2000).

The present work focused on two alternative methods for the increase of the paraffin concentration of naphtha: 1) by extraction of the aromatics with selective solvents such as sulfolane or n-methyl pyrrolidone and 2) the separation of n-paraffins from light naphtha by means of urea adduction. For the second alternative, a new experimental protocol has been developed, since light paraffins scarcely form adducts with urea.

2. EXPERIMENTAL

Two artificial naphtha feeds were used in this study for separation of the n-paraffins and aromatics. Their properties are given in Tables 1a and 1b.

Table 1a: Composition of the naphtha-1 used for aromatics extraction

	naphthenes	iso-paraffins	n-paraffins	cyclic olefins	iso-olefins	n-olefins	aromatics
C3	0	0	0	0	0	0	
C4	0	0	0	0	0	0	
C5	0	0	0	0	0	0	
C6	0.99	0	0.08	0	0	0	0.32
C7	12.59	7.55	9.51	0	0	0	2.9
C8	12.15	9.5	8.05	0	0	0	4.59
C9	8.02	8.12	5.07	0	0	0	2.33
C10	2.24	3.65	1.23	0	0	0	0.08
C11	0.12	0.31	0.57	0	0	0	0
total	36.11	29.14	24.51	0	0	0	10.23

Table 1b: Composition of the naphtha-2 used for n-paraffins extraction

	naphthenes	iso-paraffins	n-paraffins	cyclic olefins	iso-olefins	n-olefins	aromatics
C3	0	0	0.07	0	0	0	0
C4	0	0.09	0.11	0	0	0	0
C5	0	2.75	4.52	0	0	0	0
C6	0.11	5.90	11.22	0	0	0.03	0
C7	0.34	8.31	14.67	0	0	0.02	0
C8	0.47	9.38	15.38	0	0	0.04	0
C9	0.32	7.45	11.76	0	0	0	0
C10	0	0.63	6.25	0	0.04	0	0
C11	0	0	0.16	0	0	0	0
total	1.23	34.51	64.13	0	0.04	0.09	0

2.1 Liquid-Liquid extraction of aromatics from naphtha-1

For the extraction of aromatics from naphtha, two solvents were tested, sulfolane and n-methyl pyrrolidone, at different solvent to naphtha ratio. In each case, in a conical flask a proper amount of naphtha was weighed and then the solvent was added. The solution was heated mildly (up to 60°C) and was maintained under continuous stirring for 1h. Afterwards, the two phases were separated and the aromatics content of the naphtha layer was determined by gas chromatography.

2.2 Formation of n-paraffins/urea adducts from naphtha-2

The urea separation procedure followed was a modification of a previously published method of our laboratory, regarding the separation of n-paraffins and iso-paraffins from heavy FCC feedstocks (Lappas et al., 1997, Lappas et al., 1997). The modification of the method was necessary, since the naphtha sample in question consisted mainly of light hydrocarbons, having up to 11 carbon atoms. Most of the experimental work focused on finding a suitable mixture of solvents that would allow the dissolution of urea, without greatly interfering with the formation of the helices that would accommodate the n-paraffin molecules. The experimental procedure can be roughly divided in two stages. At the first stage, 5g of naphtha were weighed and added under magnetic stirring at 60°C, to a solution of urea in 25mL of a suitable solvent. The temperature was kept constant for 0.5h and then the solution was allowed to cool to room temperature, under continuous stirring for 1.5h. The urea – n-paraffin adduct, that should be formed during this time, was forced to precipitation by rapid cooling of the solution to 10°C. This temperature was kept constant for another 0.5h, under continuous agitation. At the second stage, the solid precipitate was filtered off under vacuum and washed with 20mL of a suitable solvent. Afterwards, the precipitate was collected and diluted in warm water. The extracted paraffins appeared as a separate phase. In order to achieve better separation, the aqueous solution was further extracted with a suitable solvent. The organic fractions were pooled, dried with Na₂SO₄ and finally the solvent was evaporated under reduced pressure. The extract was collected, weighed and analyzed by gas chromatography (PIONA). It should be stressed that the naphtha sample was used without previous pretreatment.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Extraction of aromatics with organic solvents

Sulfolane is an aprotic organosulfur compound, that has been used extensively for the extraction aromatic compounds, especially from hydrocarbon mixtures. For the extraction of the aromatics fraction from naphtha-1, different ratios of sulfolane to naphtha-1 were employed and in particular, 2:1, 3:1, 4:1, 8:1 and 10:1. The two liquids were mixed under continuous stirring and with slight heating in order to aid the distribution of the aromatics. The separation of the two phases was spontaneous with a clear interface. The naphtha-1 phase was retrieved and analyzed by gas chromatography for its aromatic content. As presented in Figure 1, the increase in the sulfolane to naphtha-1 ratio, led to a decrease in naphtha-1's

aromatic content, but did not affect the concentration of naphthenes, thereby proving the selectivity of the solvent.

For comparison purposes, n-methylpyrrolidone (n-MP) was also employed for the extraction of aromatics. In this case, the increase in temperature led to complete miscibility of the two phases and therefore all the extractions were conducted at room temperature. It should also be noted that naphtha-1 and n-MP are partially soluble and therefore, the use of increased volumes of solvent was not acceptable as it resulted to a homogeneous solution. The highest naphtha-1 to n-MP ratio where there was easy separation of two distinct phases was 1 to 3. At the 1 to 5 ratio, the phase separation was induced after freezing the sample for a few minutes. This solvent seems to be more efficient for the extraction of aromatics, compared to sulfolane, however, it is not as selective since there is also a marked decrease in the naphthenes content of naphtha-1 (Figure 2).

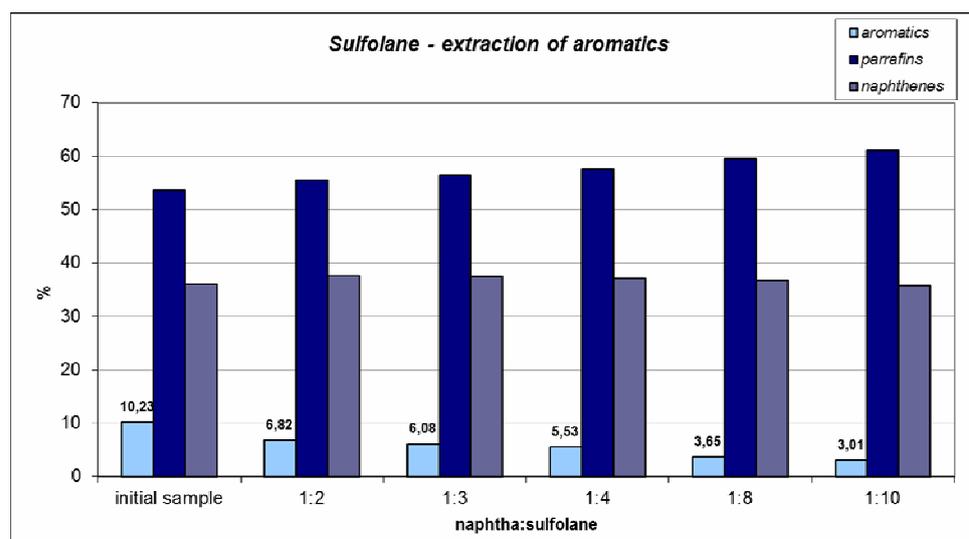


Figure 1 : Effect of naphtha-1 to sulfolane ratio on the aromatic content of naphtha-1

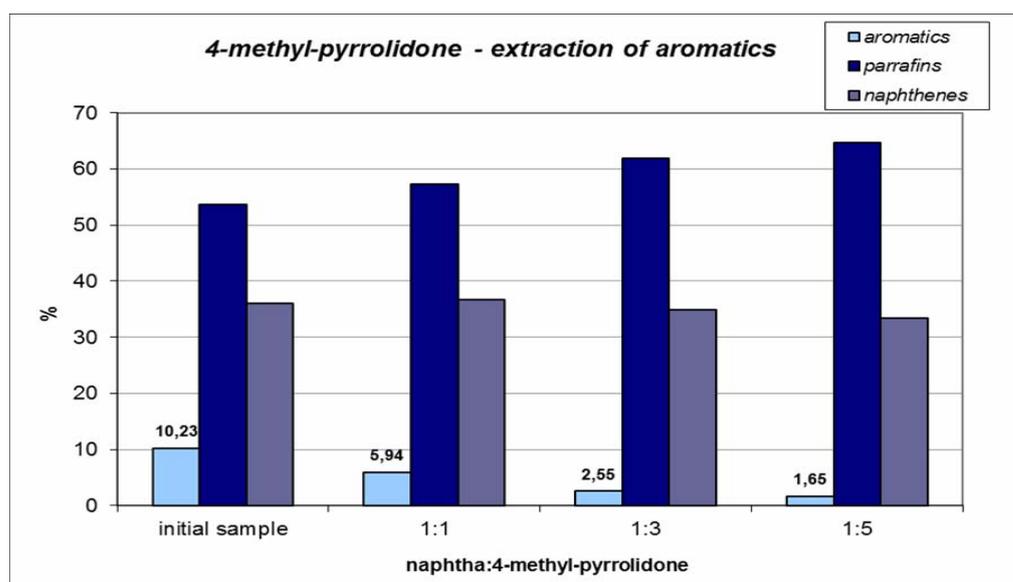


Figure 2 : Effect of naphtha-1 to n-MP ratio on the aromatic content of naphtha-1

3.2 Extraction of the n-paraffin fraction

At first, the protocol previously reported by Lappas et al. (1997) was employed for the extraction of n-paraffins from naphtha-2, but since small-chain n-paraffins do not form adducts with urea easily, the separation achieved was not satisfactory. It was assumed that the hydrogen bonding capacity of MeOH might interfere with the formation of the adducts. Therefore, since urea is a polar compound, it was attempted to replace MeOH with another polar solvent that would not have the ability to form hydrogen bonds, and for this reason THF and CHCl₃ were selected. The use of THF was rejected after two trials, as urea is almost insoluble in it and even the addition of small volumes of MeOH did not assist urea's dissolution, meaning that an effective formation of adducts could not occur. In CHCl₃ urea presents some solubility and therefore in order to enhance its solubility the addition of a small volume of MeOH was necessary. Initially, 5mL of MeOH were added to 20mL of CHCl₃, and to this solution 3g of urea were added. The extraction of the adducted n-paraffins was performed with hexane and therefore quantitative results could only be obtained for paraffins higher than hexane. As is reported in Table 2, some extraction of n-paraffins occurred and subsequently it was attempted to increase the amount of urea, up to three times the amount of sample. The results demonstrated that 6g of urea for 5g of naphtha-2 offered the best separation.

Table 2: Recovery of n-paraffins with C7 to C11 with CHCl₃

	<i>CHCl₃ 20mL + MeOH 5mL</i>			
	3g urea	6g urea	10g urea	15g urea
	% recovered			
C7	4.22	3.04	2.91	2.69
C8	6.16	7.31	7.19	5.46
C9	17.79	22.29	17.62	10.66
C10	34.52	41.24	29.49	15.41
C11	3.86	3.81	2.43	1.60
<i>Overall recovery of paraffins</i>	8.8	10.6	8.5	5.4
<i>n-Paraffins in urea extract</i>	98.58	98.53	95.07	93.59
<i>n-Paraffins in residue</i>	68.21	68.59	66.04	66.68
<i>iso-Paraffins in urea extract</i>	1.01	1.32	4.70	5.91
<i>iso-Paraffins in residue</i>	30.92	30.22	33.05	31.89

The results indicate that there is a maximum amount of urea that can be used for the n-paraffin separation since beyond that the recovery rate reduces.

The low overall recovery percentage was attributed to the limited solubility of urea to CHCl₃. In addition to that, the large scale use of chlorinated solvents is unfavorable, and for these reasons CHCl₃ was replaced by ethyl acetate (EtoAc). As is evident from Table 3, the overall recovery of the n-paraffin fraction increased to 17.1%, along with the individual recovery of n-paraffins with C7 to C11.

Table 3: Recovery of n-paraffins with C7 to C11 with EtoAc

	<i>EtoAc 20mL + MeOH 5mL</i>	
	3g urea	6g urea
	% recovered	
C7	1.66	3.54
C8	3.81	13.50
C9	15.84	38.71
C10	35.62	60.89
C11	9.11	5.09
<i>Overall recovery of paraffins</i>	7.7	17.1
<i>n-Paraffins in urea extract</i>	98.52	98.72
<i>n-Paraffins in residue</i>	64.28	54.32
<i>iso-Paraffins in urea extract</i>	0.57	1.14
<i>iso-Paraffins in residue</i>	34.32	43.31

The next step was the increase of the MeOH volume to 10mL considering that a better dissolution of the urea, might increase the adduct formation.

The increase of the overall recovery was in fact marginal, up to 17.9%. hexane as an extraction solvent for these low molecular weight n-paraffins was not considered very suitable, due to its high boiling point thus contributing to lower recoveries of the n-paraffins, due to prolonged evaporation under reduced pressure. Hence, following the establishment of the first stage of the adduct formation procedure, was the development of an extraction protocol of the adducted n-paraffins. To this end, solvents with lower boiling points were tested, such as petroleum ether, diethyl ether and pentane. The evaporation of these solvents can be performed under reduced pressure, without the need of heating, and consequently the recovery rate of the n-paraffins is enhanced. The results are presented in Figure 3.

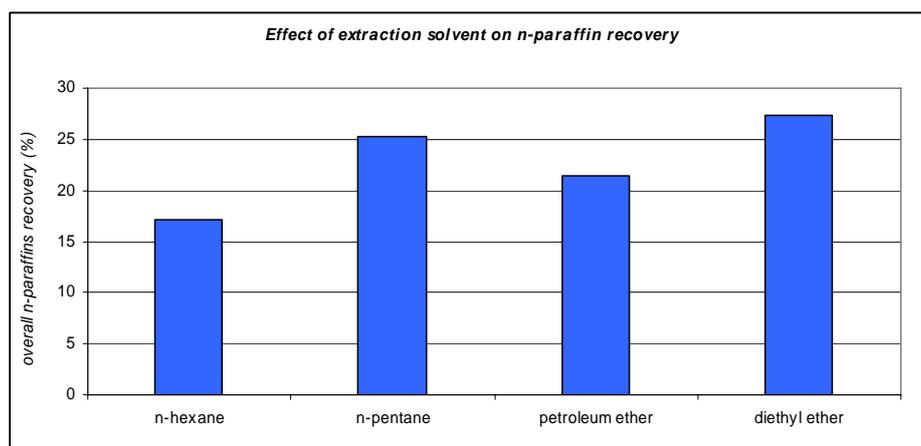


Figure 3 : Effect of the extraction solvent on overall n-paraffin recovery

The use of these solvents improved considerably the recovery rate of the n-paraffin fraction, with pentane and diethyl ether producing the best results. However, some residue solvent inevitably remains in the extract, and since oxygenates are not desirable in a naphtha-2 fraction, C_5H_{12} was chosen as a suitable solvent. At this point, after having established a more efficient liquid-liquid extraction procedure, the effect of the MeOH volume at the first stage of the procedure was re-examined. The effect was examined on three levels of MeOH volume: 5mL, 10mL and 15mL, added to 20, 15 and 10mL of ethyl acetate respectively. The results are presented in Figure 4.

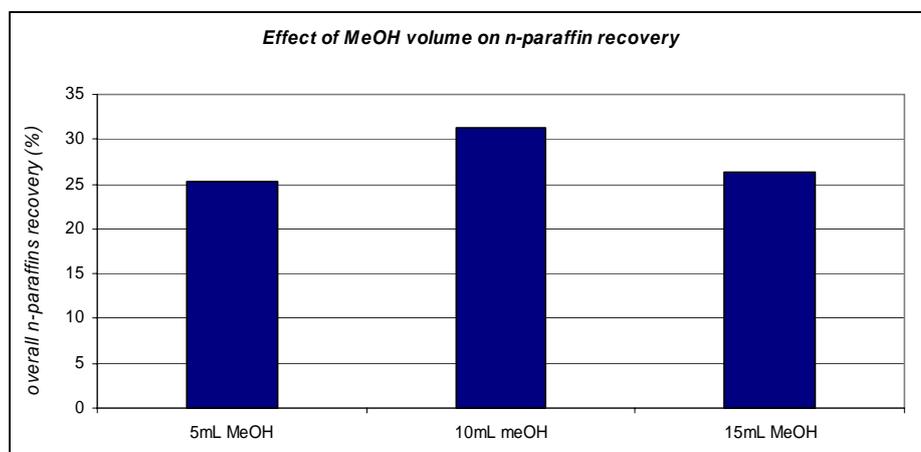


Figure 4 : Effect of the MeOH volume, at the first stage, on n-paraffin recovery using C_5H_{12} as an extraction solvent

The results indicate that up to 10mL of MeOH at the first stage of the process facilitate the n-paraffins extraction, but a further increase of its volume has the adverse effect.

Concluding, the final extraction protocol proposed is:

Addition of 5g of naphtha-2 in a solution consisting of 15mL EtoAc, 10mL MeOH and 6g urea. Addition should be done under continuous stirring at 60°C. These conditions are to be maintained for 0.5h, after which stirring is continued for 1.5h with slow cooling of the solution to room temperature. Then, the solution temperature is reduced to 10°C and maintained at this temperature for another 0.5h. The precipitate is recovered by filtration under vacuum, washed with 10mL of pentane and then diluted to 50mL of warm water. The n-paraffin fraction is recovered by liquid-liquid extraction with 80mL of n-C₅H₁₂. The organic solvent is evaporated under reduced pressure, and the n-paraffin fraction is collected and analysed.

This experimental protocol was employed to a sample of 20g of naphtha-2, in order to evaluate the repeatability of the proposed method. The results are presented in Table 4.

Table 4: Results of the proposed extraction protocol employed to 20g of naphtha-2

	<i>EtoAc 15mL + MeOH10mL</i>
C6	4.87
C7	18.85
C8	44.14
C9	66.24
C10	83.16
C11	10.84
<i>Overall recovery of paraffins</i>	35.2
<i>n-Paraffins in urea extract</i>	91.35
<i>n-Paraffins in residue</i>	34.58
<i>iso-Paraffins in urea extract</i>	4.39
<i>iso-Paraffins in residue</i>	31.88

3.3 Extraction of the iso-paraffin fraction

At the end of the first stage of the experimental procedure described above, after the filtration of the precipitate under vacuum, the filtrate received is a fraction enriched in iso-paraffins that can be collected after the evaporation of the solvents. However, the inherent volatility of both the sample and the solvents used causes great losses during the filtration under vacuum, and as a result the recovery of the extracted naphtha-2 is low. Plain filtration is not advisable at this stage since it is very slow and does not eliminate the losses due to evaporation. Additionally, the washing of the precipitate is not efficient and as a result some iso-paraffins are transferred to the n-paraffin extract thereby decreasing its purity. In order to overcome this problem centrifugation could be used for the separation of the precipitate, and this is proposed to be the next step of our work.

4. CONCLUSIONS - SUGGESTIONS

The extraction of aromatics from naphtha was attempted by means of two commercially used organic solvents. N-MP is more effective for the extraction of aromatics at smaller ratio, compared to sulfolane, however it is not equally selective. Additionally it is partially miscible with naphtha, therefore sulfolane is more appropriate as a solvent. With Sulfolane we can remove the aromatics in naphtha from 10% to about 3%.

An extraction protocol for the recovery of small n-paraffins with 6 to 11 carbon atoms has been presented. The results verify the literature supporting that the adduction of n-paraffins with more than 8 carbon atoms is more efficient, but under the conditions employed the adduction of shorter n-paraffins has also been made possible. The recovery of the iso-paraffin fraction was not as efficient due to losses at the filtration step. However, these losses might be eliminated if centrifugation instead of vacuum filtration is employed.

5. LITERATURE

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