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STUDY ON DEASPHALTING AND DEMETALATION OF HEAVY PETROLEUM RESIDUE:

PART I

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ABSTRACT

Nowadays attention is focused on the production of fuel ,conform the standered specification ,wich to be friendly environment .This lead to be enconrragement the research in the field of convert the heavy petroleum products into clean fuels. Most of the egyptian oils are quit heavy with poor yield and quality of light distillate. Solvent deasphalting process permits practically recovering much higher heavier oils and extracts well the high purity deasphalting oil from atmospheric or vacuum residues.

In this study, the effect of temperature and solvent feed ratio on the quality of the vacuum petroleum residual have been investigated, solvent deasphalting process was carried out in a batch autoclave at different temperatures 40°C, 60°C and 80°C using basic n-paraffins solvent (n-pentane) at n- pentane/ residue ratios 3:1, 5:1 and 8:1 with auxiliary polar solvent N-methyl 2-pyrolidone (NMP) at different NMP/ residue ratios 0.25:1, 0.50:1, 1:1 and 2:1

Treating vacuum petroleum residues with n-pentane and NMP results in a deasphalted oil with reduced amounts of heavy metals and conradson carbon.

The most promising conditions of deasphalted oil is obtained by using n-pentane ratio of 8:1 and NMP ratio of 0.5:1 at 80°C

INTRODUCTION

In recent years, demand for heavy fuel has decreased significantly while the need for light and middle distillates has moved in the opposite direction. At the same time, environmental concerns have increased, resulting in more rigorous specifications for petroleum products including fuel oils. These trends have emphasized the importance of processes that convert the heavier oil fractions into lighter and more valuable clean products [1 - 4] .

As the refiners increase the proportion of heavier, poor quality crude in their feedstocks, the need grows for effective processing methods to treat the fractions containing increasingly higher levels of sulfur, metals and conradson carbon residue (CCR). Asphaltene [5 - 7]: the n-heptane-insoluble heavy fraction of crude oils, constitute one of the primary components of crude oil, and, as such, are of considerable interest [8 - 11]. Asphaltenes provide very low cracking yields and are of low economic value, they are relatively high in undesired heteroatoms (S, O, N), and they contain heavy metals such as Ni and V, which can poison catalysts. They have been the subject of wide range studies to elucidate their chemical structure but these studies have been only partially successful, primarily because the asphaltenes exhibit significant complexity and some variability.

Solvent deasphalting process permits practically recovering much higher heavier oils and extracts well the high purity deasphalting oil (DAO) from atmospheric or vacuum residues. It is well known that asphaltene and resins, in heavy oils are the non ideal compositions to upgrade. These are a solubility class of materials that precipitate from the oils when disturbing the solution equilibrium by the additives of selected solvents at the same conditions. Undesired metal containing and sulfur components are also removed during the deasphalting processes. [12 - 15]

The aim of our work is to develop deasphalting and / or demetalation scheme by using basic paraffinic solvent (n- pentane) with polar solvent N- methyl pyrrolidone (NMP). In order

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to produce deasphalted oil,such deasphalted oil may be economically used in a catalytic-cracking process.

Experimental part

Feedstock: The vacuum petroleum residues were obtained from Suez Petroleum Co. and have the characteristics shown in Table 2.

1-Deasphalting conditions: The vacuum residues were subjected to solvent deasphalting at different temperatures 40°C, 60°C and 80°C using different n- pentane to residue ratio 3:1, 5:1 and 8:1 with polar solvent N- methyl 2-pyrrolidone (NMP)to residue ratio 0.25:1, 0.5:1, 1:1 and 2:1.

Deasphalting solvents: n- pentane and N- methyl -2-pyrrolidone (NMP) were used as deasphalting solvents.

Deasphalting procedure: Deasphalting process was conducted in a batch reactor which was composed of a magnetically stirred autoclave heated by digital controller.
Predetermined quantities of the feed mixtures were taken into the autoclave and stirred thoroughly for one hour to ensure perfect mixing, then allowed to settle four hours for complete separation. The two phases were taken out separately. The deasphalted oil and the asphalt residue were recovered by atmospheric distillation followed by vacuum distillation at 10 mmHg the product, was analyzed according to IP [16] and ASTM [17] standard methods.

RESULTS AND DISCUSSION

I -Solvent deasphalting

Table (1) indicates the properties of vacuum residual oil under investigation.
The deasphalting process occurs at different temperatures 40°C, 60°C and 80°C using basic n-paraffins solvent (n-pentane) at n pentane /residue ratios 3:1, 5:1 and 8:1 with auxiliary polar solvent NMP at different NMP/residue ratios 0.25:1, 0.50:1, 1:1 and 2:1.

The data are reported in Tables (2, 3 and 4) and Figures. (1, 2, 3 and 4). It is well known that the temperature is one of the important variables in the liquid extraction processes. Accordingly, it seems that there is an optimum temperature range for any used solvent within which it is desirable to operate. It is of importance to study the effect of variation of temperature on the efficiency of deasphalting process. In this study, the effect of temperature and solvent feed ratio on the quality of the product have been investigated. In scope of reducing the ratio of n- pentane used we study the effect of addition of polar solvent NMP to the n-pentane. Increasing the NMP ratio lead to increase of oil yield and viscosity, conradson carbon increases related to increase in viscosity, this may be explained by the transfer of NMP and heavy hydrocarbons soluble in it to the n- pentane rich phase and it depends on the mutual solubility of the solvents and residue.
On the other hand, increasing the NMP ratio lead to decrease the asphalt yield.

It can be seen from Tables (2, 3 and 4) and Figures. (1, 2, 3 and 4) that with decreasing the temperature the oil yield increases in different of NMP and n-pentane ratios, at the same time with increasing the temperature, selectivity of n- pentane increases which lead to decrease the oil yield and improvement of its quality.

At lower temperature (40°C) and solvent ratio of n-pentane (3:1) n-pentane become less selective and due to the co-solvent effect of the oil dissolved in n-pentane. High yield of oil was obtained but with inferior quality.

This may be attributed to the presence of high molecular weight aromatic hydrocarbons as indicated with high conradson carbon, high viscosity and high metal level. It is found that at temperature of 60°C increasing pentane ratios from 3:1 to 8:1 leads to increase the oil yield and improvement of its quality . It is clear that the optimum conditions of deasphalted oil is obtained by using n-pentane ratio of 8:1 and NMP ratio of 0.5:1 at 60 °C.

Table (1) Characteristics of vacuum residue obtained from Suez Petroleum Co.

Characteristics	Vacuum residue
Specific gravity at 70°C	0.993
Flash point	Over 320°C
Conradson carbon Residue	18.75
Sulfur content wt%	4.63
Asplaltene content wt%	6.4
Ni ppm	138.5
V ppm	164.5
Ni+V ppm	303

Table 2: Properties of the vacuum residue after treatment with (3:1) n-pentane at different temperature and NMP ratios

n-pentane/ Residue Ratio vol.	3									
Temperature °C	40					60				
NMP/Residue Ratio vol.	0	0.25	0.50	1	2	0	0.25	0.50	1	2
Oil Yield % g	22	44	46	47	48.5	9.3	23	25	27	33.5
Density at 20°C ASTM D-1298	0.9160	0.9201	0.9331	0.9374	0.9432	0.9160	0.9223	0.9282	0.9318	0.9390
Viscosity at 100°C cSt IP-71	65	116	121	123	131	50	72	83	92	143
Viscosity index	84	83	82	79	77	84	84	81	81	80
Conradson carbon wt.% ASTM D-189	2.8	4.2	4.8	4.8	4.9	2.2	2.8	3.3	4.1	5.1
(N1+V) ppm ASTM D811-48	262	266	268	272	285	258	264	270	285	290
Asphalt yield % g	75	52.5	50.5	49.5	48	87.5	73.5	72	69.5	63
Softing point °C ASTM D36	48	64	54	51	54	38	45	42	43	38

Table 3: Properties of the vacuum residue after treatment with (5:1) n-pentane at different temperature and NMP ratios

n-pentane/ Residue Ratio vol.	5														
Temperature °C	40					60					80				
NMP/Residue Ratio vol.	0	0.25	0.50	1	2	0	0.25	0.50	1	2	0	0.25	0.50	1	2
Oil Yield % g	27.4	40	48.7	51.5	53.3	17	28	34.5	36.5	40.5	7.7	18.4	23.1	24.9	31.2
Density at 20°C ASTM D-1298	0.9201	0.9290	0.9335	0.9353	0.9407	0.9182	0.9224	0.9250	0.9276	0.9280	0.9105	0.9121	0.9151	0.9183	0.9200
Viscosity at 100°C cSt IP-71	53	87	98	102	124	47	68	76	83	87	38	48	55	64	70
Viscosity index	84	83	81	80	79	85	84	83	82	77	87	86	85	82	76
Conradson carbon wt.% ASTM D-189	2.1	3.7	3.8	4.2	4.7	1.7	2.8	3	3.1	3.2	1.4	2	2.7	2.7	3.3
(Ni+V) ppm ASTM D 811-48	194	204	214	225	238	192	202	215	257	260	192	298	207	221	225
Asphalt yield % g	69.5	56.5	48	45	43	80	68.5	62	60	56	89	78	74	71.5	65.5
Softing point °C ASTM D36	49.5	58	67	68	70	47.6	49	51	54	65	32.6	37	45	46	48

Table 4 : Properties of the vacuum residue after treatment with (8:1) n-pentane at different temperature and NMP ratios

n-pentane/ Residue Ratio vol.	8														
Temperature °C	40					60					80				
NMP/Residue Ratio vol.	0	0.25	0.50	1	2	0	0.25	0.50	1	2	0	0.25	0.50	1	2
Oil Yield % g	29.4	46.6	50	51.7	51.7	23	32.5	38.3	45.5	48.3	10.5	13.2	19.2	26.6	31.3
Density at 20°C ASTM D-1298	0.9251	0.9283	0.9312	0.9316	0.9320	0.9205	0.9234	0.9263	0.9280	0.9297	0.9132	0.9161	0.9171	0.9173	0.9185
Viscosity at 100°C cSt IP-71	65	91	93	94	95	53	68	74	85	91	50	51	55	59	67
Viscosity index	85	81	80	79	77	85	83	82	82	78	83	82	80	79	77
Conradson carbon wt.% ,ASTM D-189	2.2	3.2	3.3	3.4	3.8	2.7	3	3.2	3.3	3.6	1.6	2.1	2.2	2.3	2.6
(N1+V) ppm ASTM D 811-48	165	170	176	181	188	144	151	163	172	190	130	145	160	185	198
Asphalt yield % g	67.5	50	47	45	45	73.5	64	58.5	51	48.5	86	83.5	77.5	70	65.5
Softing point °C ASTM D36	48	66	74	72	68	44	52	66	68	67	33.5	41	48	48	45
Heavy metal Removal	83.94	73.77	70.9	69.1	67.81	89.03	73.8	80.9	74.1	79.6	78.48	75.51	70.86	63.86	56.07

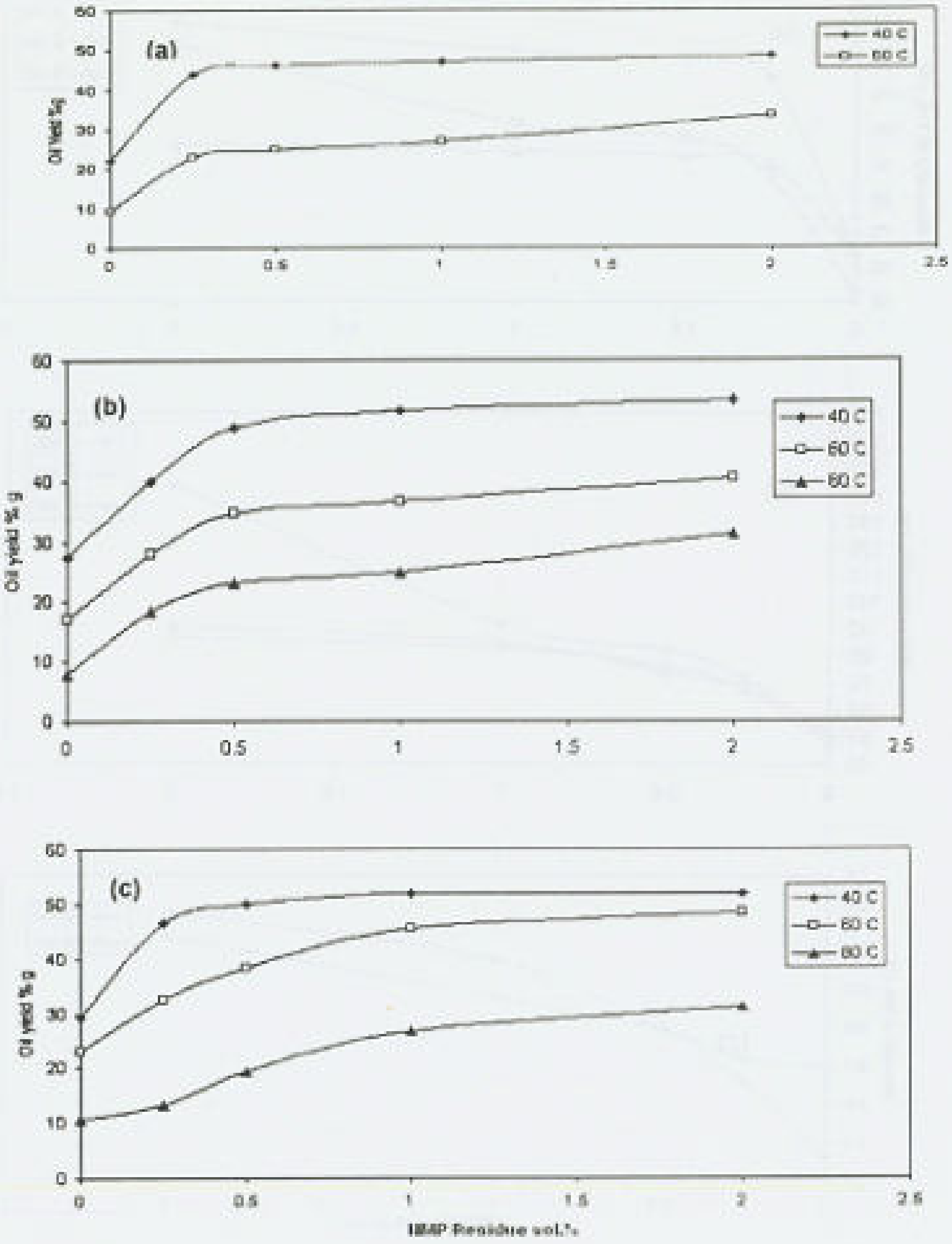

Fig. (1) Relation between yield and NMP/Residue at different n-pentane ratios vol
(a), C_5/ Residue Ratio vol 3:1
(b), C_5/ Residue Ratio vol 5:1
(c), C_5/ Residue Ratio vol 8:1

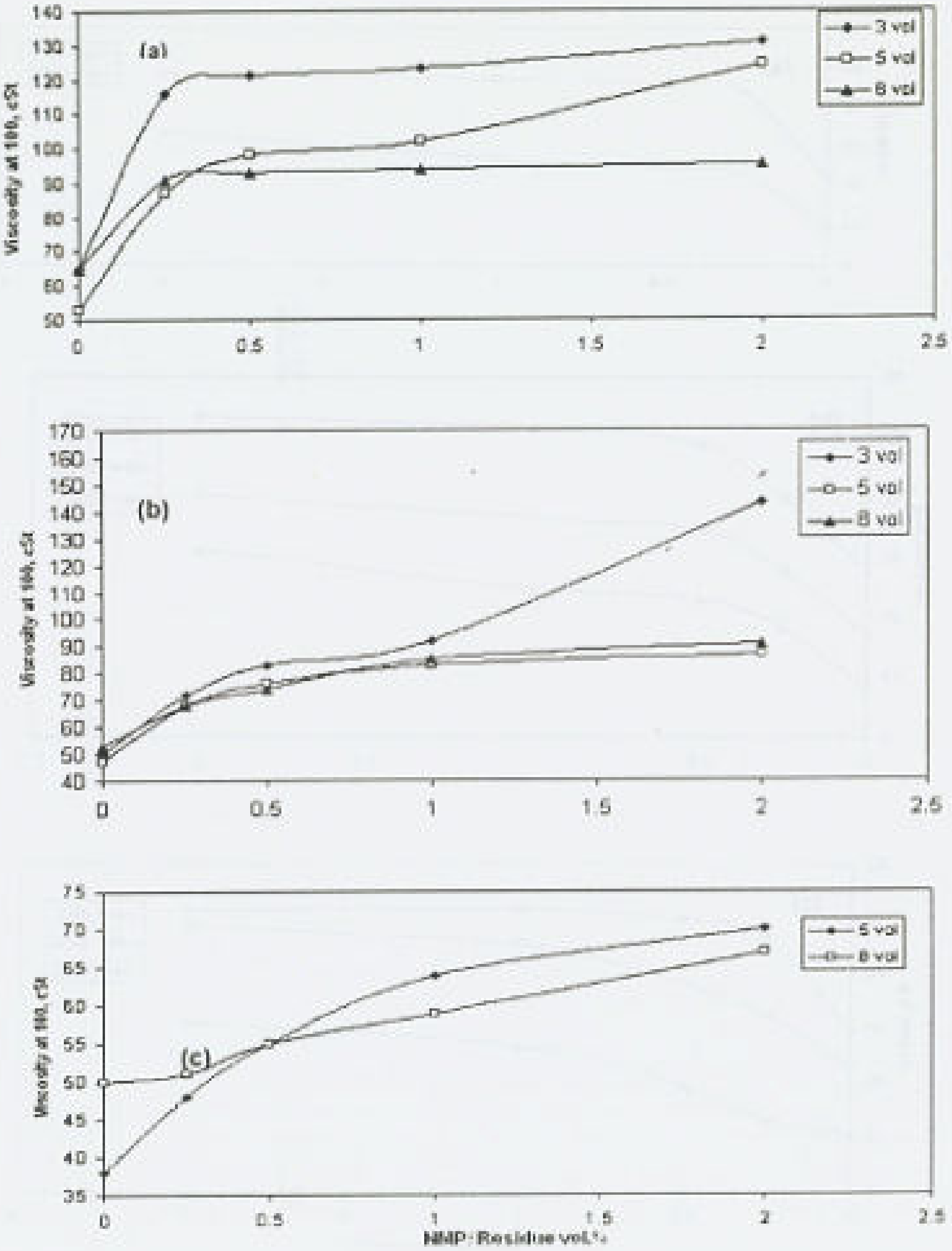

Fig. (2) Correlation between NMP/Residue and viscosity at 100, cSt at differen temperature
(a) Temp. 40°C
(b) Temp. 60°C
(c) Temp. 80°C

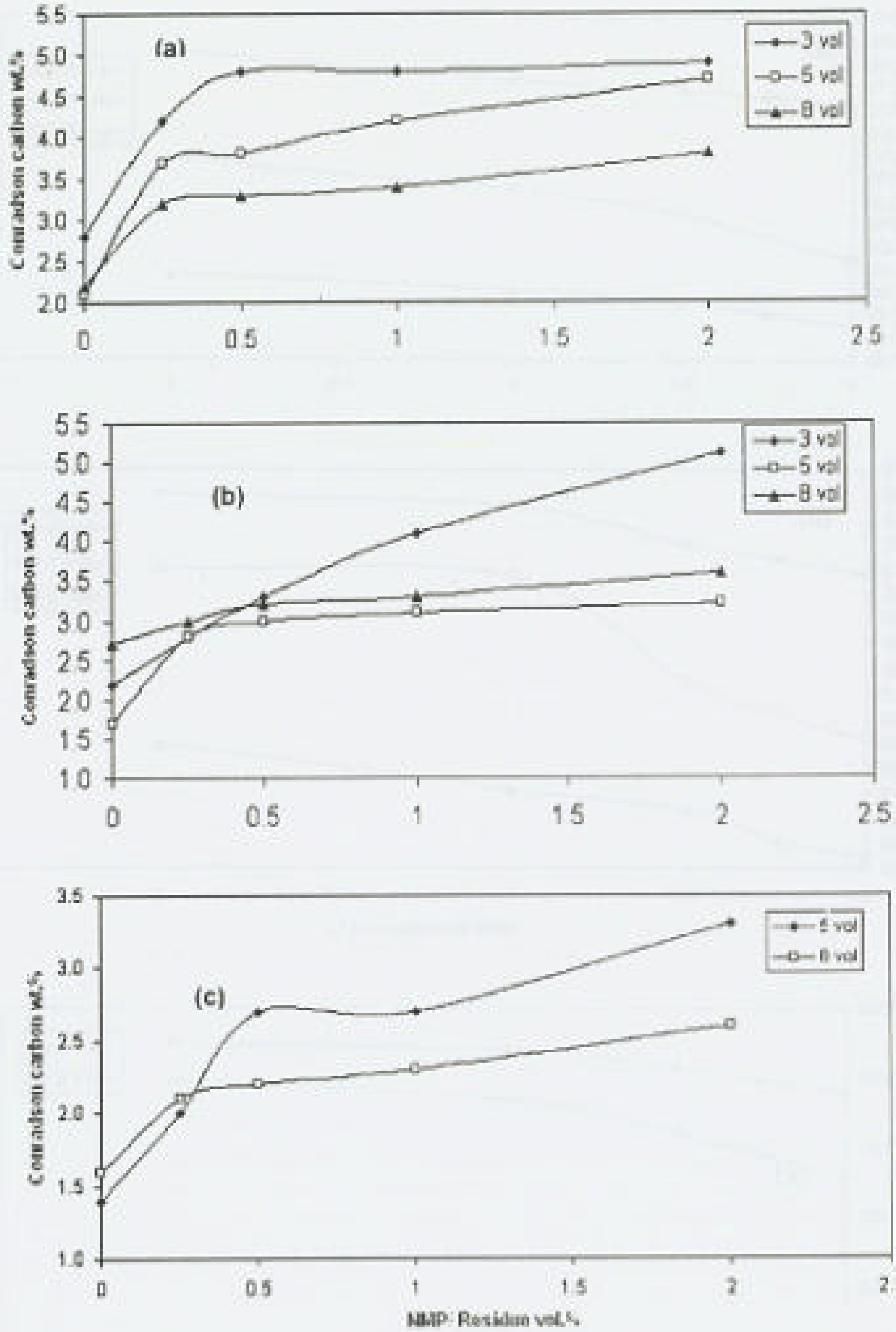

Fig. (3) Correlation between NMP/Residue and Conradson carbon at 100, cSt at differen temperature
(a) Temp. 40°C
(b) Temp. 60°C
(c) Temp. 80°C

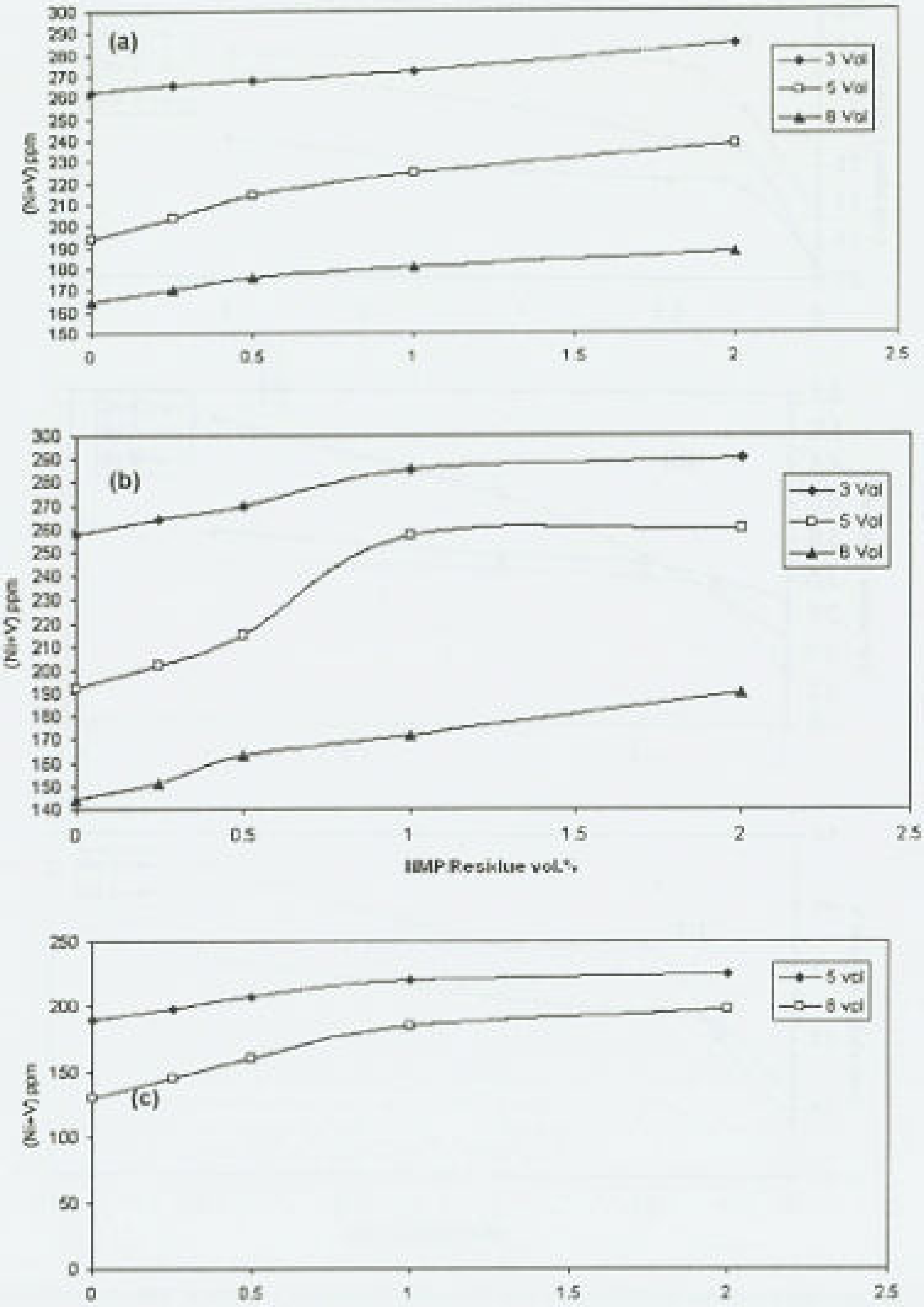

Fig. (4) Relation between metal content (Nii+v) yield and NMP/Residue at different n-pentane ratios vol.
(a) Temp 40°C
(b) Temp. 60°C
(c) Temp. 80°C

CONCLUSION

The results of this study can be concluded that:-

- Increasing of n-pentane ratio and temperature lead to increasing selectivity of the solvent and improvement of the oil quality.
- In the case of decreasing of n-pentane ratio and temperature the oil yield high but its quality inferior.
- Treating vacuum petroleum residues with n-pentane and NMP results in a deasphalted oil with reduced amounts of heavy metals and conradson carbon. Therefore, the optimization of the deasphalting process may vary as a function of the conversion process applied to such feedstocks. Such deasphalted oil may be economically used in a catalytic-cracking process.

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دراسة على إزالة المعادن والأسفلتينات من المتخلف البترولى الثقيل

الجزء الأول

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يعتبر الحفاظ على البيئة من التلوث هو الشغل الشاغل لجميع الدول ومن أجل ذلك تم وضع مواصفات عالمية لنوعية الوقود البترولى لحماية البيئة من أخطار التلوث وقد أدى ذلك الى تشجيع البحوث فى مجال تحويل المواد البترولية الثقيلة الى وقود نظيف وذلك بإزالة الأسفلت و كذلك الهدرجة

ومن المعروف أن المتخلف البترولى الثقيل يحتوى على نسبة عالية من المعادن والمواد الأروماتيه متعددة الحلقات و تناول هذه الدراسة طرق معالجة المتخلف البترولى الثقيل عن طريق عمليات الأستخلاص بالمذيبات.

وقد استخدم فيها خليط من مذيب البنتان من نسب مختلفة من مذيب ن- الميثيل بيرولودن عند درجات حرارة ٤٠م، ٦٠م و ٨٠م وقد تم دراسة تأثير التغير فى درجات الحرارة ونسب المذيبات على الخواص العامة للزيت والأسفلت الناتج وقد خلصت النتائج الى أن المعالجة باستخدام ن بنتان بنسبة ٨:١ والميثيل بيرولودن بنسبة ٥:١ عند ٨٠م يؤدى الى خفض نسبة المعادن والمواد الكربونية فى المتبقى الثقيل بحيث يمكن الأستفادة منه بعد ذلك بتحويله الى منتجات خفيفة عن طريق عمليات التكسير.

مما سبق يتضح أن اضافة المذيبات القطبية مثل مذيب ن الميثيل بيرولودن مع مذيب ن بنتان فى عمليات ازالة الأسفلت يؤدى الى تحسين فى خواص الزيت الناتج وتقليل نسبة المذيب المستخدم