Desulfurization of Libyan Fuel Oil by Solvent Extraction

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Abstract:

New strict environmental regulations to reduce sulfur content in liquid fuel have been established. Thiophene derivatives can be considered as the key substances to be separated from liquid fuels. This research reports the ability of the solvent extraction, in liquid-liquid single and multistage extraction steps, to remove thiophene derivatives. Four liquid solvents have been used in the extraction. These are N-methyl-2-pyrolidone (NMP), acetonitrile (MeCN), methanol (CH_3OH) and water (H_2O). This work main contribution is to provide a comprehensive and systematic equilibrium data for the extraction of dibenzothiophene (DBT), diebenzothiophene sulfone (DBTs) and their mixture respectively. An attempt to predict equilibrium extraction data was also carried out using the estimated binary interaction parameters for two liquid non-ideal phase behaviour models. These are UNIQUAC and NRTL. Such data and predictions are to the best of the author knowledge are lacking from the open literature. Predictability of NRTL and UNIQUAC temperature independent models has been evaluated and was found to be very satisfactory. Binary interaction parameters for these two models for diesel fuel constituents and solvents were estimated based on the UNIFAC whereas that for DBT–Solvent pair was estimated based on comparison of DBT compositions measured and calculated in the fuel layer.

Key words: Desulfurization, extraction, solvents, sulfur compounds and Hysys.

نزع مركبات الكبريت من النفط الخام الليبي عن طريق عملية الاستخلاص

عبدالعظيم سالم جرود
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الملخص

في السنوات الأخيرة ثم وضع قوانين بيئية صارمة لخفض نسبة الكبريت في الوقود. مشتقات الثيوفين (Thiophene derivatives)تعتبر المفتاح لفصل هذه المواد من الوقود. هذا البحث يتناول قابلية المذيبات فى الفصل للمرحلة الواحدة (Single stage) ولعدة مراحل (Multistages) لإزالة مشتقات الثيوفين واكسدة هذه المشتقات من الهيروكربونات الاروماتية بواسطة المذيبات القطبية. (Polar solvent) أربع أنواع من المذيبات استعملت في الاستخلاص. وهى الميثانول (CH_3OH)، اسيتونيتريل (MeCN) ، NMP و الماء(H_2O) المساهمة الرئيسية في هذا البحث هي تزويد بيانات اتزان شاملة ومنظمة لاستخلاص داى بينزوثيوفين (DBT) و داى بينزوثيوفين سلفون (DBTS) وخليط منهما على التوالى. وكذلك محاولة التنبؤ بمتغيرات التداخل (Binary interaction parameter) لسائلين(Liquid-liquid) سلوكهما غير مثالى(Non ideal) ومقارنتها بالمتغيرات العملية من حيث معرفة مكونات DBT وباستخدام معادلتين هما: Uniquac, وNRTL
تجارب الاستخلاص لمركبات الكبريت كانت عند 25°م عندما ثم استخدام MeCN ، NMP ، H_2O اما عند استخدام الميثانول فكانت عند 25° م ، 40° م.
اداء وفعالية الاستخلاص عند ظروف التشغيل المختلفة ثم حسابها، حيث وجد ان تاثير درجة الحرارة على استخلاص الميثانول ضئيل جدا بين 25° م ، 40° م ومعدل نزع الكبريت واطىء. وكذلك وجد ان (NMP) له افضل تاثير فى نزع (DBT) من وقود الديزل عند درجة حرارة الغرفة حيث كانت كفاءة الاستخلاص 90%.
المذيبات المستخدمة نستطيع بسهولة تدويرها او اعادة استعمالها بالتبخير او التقطير(Evaporation or distillation)
الاستخلاص دو الست مراحل كان فعالا جدا فى استخلاص (DBT) باستعمال الميثانول.
الهيروكربونات المفقودة ومعدل نزع الكبريت كلاهما يؤثر على(Solvent effectiveness factor K) وهو متغير يعتمد على عدد المراحل ونسبة المذيب الى الوقود ونوع المذيب المستخدم.
معامل الفاعلية (K) لاستخلاص الميثانول يكون فى المرحلة الواحدة أفضل من متعدد المراحل. معامل الفاعلية(K) لاستخلاص الاسيتونيتريل (MeCN) لمرحلتين(Two stages) هو 11.4 عندما كانت نسبة المذيب الى الوقود هى 3.

الكلمات المفتاحية: استخلاص النفط، نزع الكبريت، الضغط، الخصائص البتروفيزيائية

1.Introduction

Crude oil is the largest and most widely used source of energy in the world. Major portions of the crude oils are used as transportation fuels such as gasoline, diesel and jet fuel. However, (Howard F. Rase,2000, and Houalla, M., etal 1978,) contains sulfur, typically in the form of organic sulfur compounds. The sulfur content and the API gravity are two properties which have a great influence on the value of the crude oil. The sulfur content is expressed as a percentage of sulfur by weight and varies from around 0.04% in light crude oil to 5% in heavy crude oil depending on the type and source of crude oil. Sulfur compounds exist in various forms and can be classified into four main groups: mercaptans, sulfides, disulfides and thiophenes, (Walid A. Al-Naeem,2004, and (Katzer, J. R etal,1979)

Petroleum-derived middle or heavy feed stocks, such as light oil, usually contain high proportion of sulfur and nitrogen impurities (Dong, D.; etal ,1997) However, the catalysts are not active in removing refractory sulfur compounds that are satirically hindered. This is particularly true in the case of sulfur compounds like thiophenes and multi ring aromatic sulfur compounds, such as dibenzothiophene (DBT) and its derivatives, 4,6- dimethyldibenzothiophene (4,6-DMDBT), (Kabe, T.; etal,1992, and Girgis, M. J.; Gates, B. C, 1991).

In order to meet future fuel specifications, such sulfur compounds must be removed or reduced to target limits within a regulatory period. Much effort has been devoted to developing techniques that can reduce or remove such refractory sulfur compounds by oxidation/extraction and biodesulfurization, (Gutberlet, L. C.; Bertolacini, R. J.1983). In general, diesel fuel and gasoline contain 20 to 30 percent aromatics but less than 1 percent sulfur, so removing the sulfur without removing the aromatics is difficult, particularly in the HDS process which also potentially hydrogenates (saturates) aromatics. It is preferable, however, to include certain aromatic compounds such as toluene and naphthalene in the fuel as they contribute significantly to fuel quality. (A. Konig, G.;etal, 2002 and C. Song, Catal.,2003)

2. Methodology

Model compounds: Two types of sulfur model compounds are selected to evaluate the extraction of sulfur compounds. The chosen of sulfur model compounds are as follows:
Dibenzothiophene (DBT) and dibenzothiophene sulfone (DBTS).
These were supplied by Aldrich, and their characteristics and physical properties are given in Table (1).
Solvents: Methanol (CH_3OH), N-methyl-2-pyrolidone (NMP), acetonitrile (MeCN) and water (H_2O), first three were supplied by BDH Laboratory, Their specific gravity and boiling point are given in Table (1).

Table 1. physical properties of chemical materials:

Chemical materials	Physical properties					Purity by Wt%
	Formula	M.wt(g/gmol)	B. P (°C)	M. P (°C)	ρ (g/ml) @20° C	
Methanol	CH_3OH	99.8	64.65	-97.68	0.811	99.8
NMP	C5H9NO	99	205	-24	1.03	99
Acetonitrile	C_2H_3N	99.9	82	-48	0.786	99.9
DBT	$C_{12}H_8S$	98	331.45	98.67	1.125	98
DBTS	$C_{12}H_8O_2S$	97	-	231-233	-	97

M.wt=Molecular weight (g/gmol), M. P=Melting point (°C), B.P=Boiling Point (°C), ρ=Density (g/ml)

Reference diesel fuel: This diesel fuel has been used as a model for diesel fuel and it has negligible sulfur content.

A known sulfur compound such as DBT and/or DBTS is dissolved in this reference fuel. The concentration of dissolved sulfur is adjusted to be in the range of expected sulfur content in straight run gas oils or hydrotreated gas oil**.** The characteristics of the reference diesel fuel are shown in Table (2).

Table 2. Characteristics of diesel fuel

Physical property	Diesel fuel	Method
Density@15°C,Kg/L	0.7906	ASTM D 4252
Specific gravity@60/60F	0.7910	ASTM D 1298
^{0}API	47.39	ASTM D 1298
Kinematic viscosity@50^{0}C,cst	2.12	ASTM D 445
Distillation initial boiling point,°C	187	ASTM D 86
10% by volume distilled, °C	214	
20% by volume distilled, °C	225	
30% by volume distilled, °C	235	
40% by volume distilled, °C	249	
50% by volume distilled, °C	250	
60% by volume distilled, °C	255	
70% by volume distilled, °C	259	
80% by volume distilled, °C	263	
90% by volume distilled, °C	265	
Final boiling point,°C	280	
Cetane Number	76.4	ASTM D 613
Cetane Index	72.5	
Poly nuclear aromatics (PNA)	2.1%	
Total Aromatics	6.7	ASTM D2549

Sulfur measurement:

Equipment: The HORIBA Model SLFA-2100Sulfur-in-oil analyzer uses the energy-dispersive X-ray fluorescence spectroscopy method for the accurate and rapid analysis of the sulfur content of petroleum products, including fuel oil and diesel fuel. It measures a range from 0 wt % to 5 wt %, amounts of sample from 4-10cm^3, amount of sample. Figure. (1) shows the HORIBA Model SLFA-2100 used in the current research.



Figure 1. Horiba Model Slfa-2100H Sulfur-in-oil analyzer Sample cell**:**

The sample cell used for the SLFA analyzer has been specially developed for the accurate measurement of the sulfur content in fuel oil by the energy dispersive X-ray fluorescence spectroscopy method. A major part of the sample cell is made of plastic. It consists of the following parts; disposable cell, inner and outer frame of cell and cell window.

The procedure of preparing the sample cells is followed from the manual operation. The SLFA series are manufactured so that the error will be 0.03 wt % S maximum when a sample of 1 wt% S is measured.

Calibration of equipment:

The calibration of the setup is necessary to measure the sulfur of oil fractions. The calibration requires more than one sample of which sulfur concentration is known; this is called a standard sample.

In general, to measure the sulfur content in fuel oil, the following two types of standard samples are to be used.

I. Standard samples prepared by mixing tetralin, decaline and dibutyldisulfide (DBDS).
II. Standard sample for sulfur content in oil, verified by the Japanese petroleum society.

Report the results as the total sulfur content, mass % and state that the results were obtained according to test method ASTM D 4294.

Setup of extraction experiments:

A 250 cm^3 two jacketed flask fitted with a mechanical stirrer and a thermocouple were used to carry out the extraction process. The

temperature is controlled by passing water through the shell surrounding the flask. The experimental equipment used in this study was erected in the laboratories of the Petroleum Research Center (PRC). Figure (2) is a photograph of assembled apparatus used for extraction experiments.

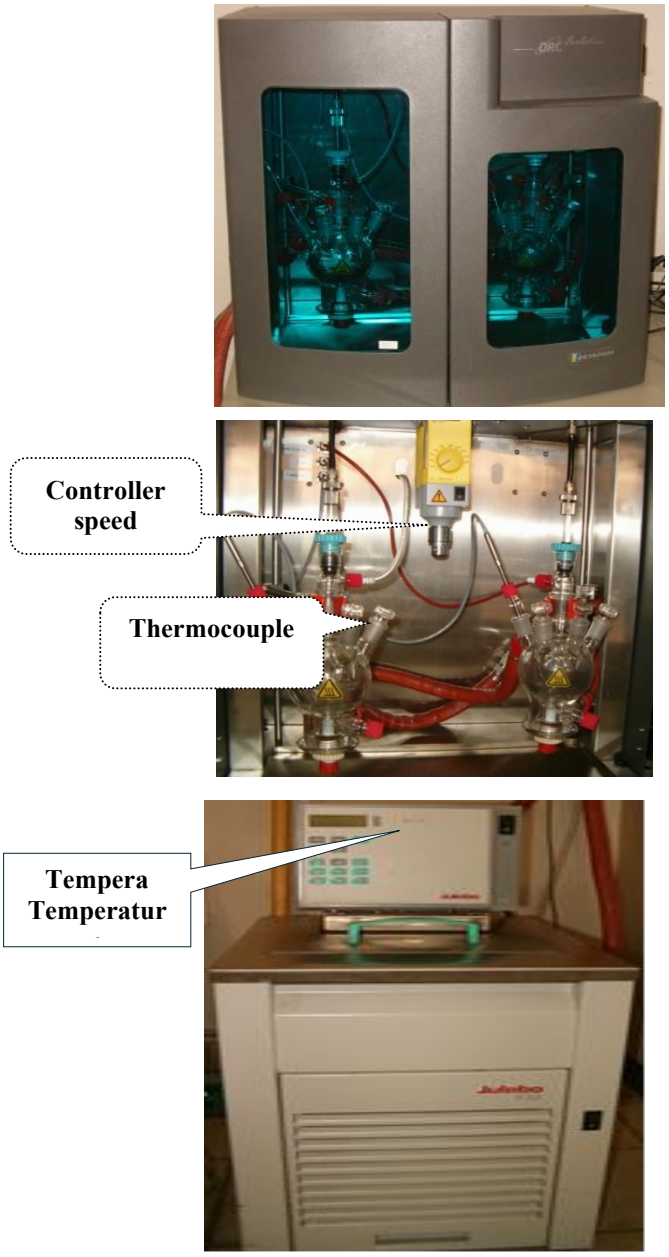


Figure.2. Extraction, setup experiment

Procedure of extraction experiments:

The extraction of sulfur compounds from diesel fuel by different solvents: methanol, acetonitrile, NMP and water at different operating conditions such as concentrations of sulfur in oil, solvent to oil ratio, temperature, time and mixing speed. The extraction of sulfur from compound diesel sample has been carried out in the extraction setup described above. The extraction experiment was performed at 25 ^{0}C with all solvents and in addition at 40^{0}C when methanol is used.

Multistage extraction operation was examined with successive six stages using methanol as a solvent.

The phases are then allowed to separate in a separation funnel as in Figure (3) and their volumes are measured, the hydrocarbon phases were washed with distilled water and then analyzed for their sulfur content.

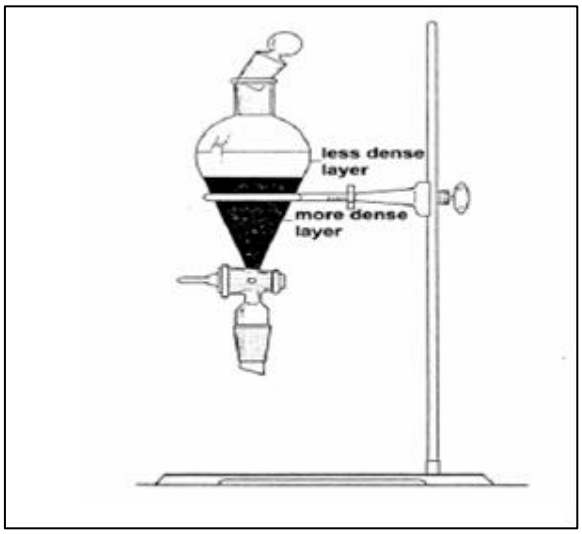


Figure. 3. Separation funnel

Reproducibility:

Reproducibility of extraction:

The reproducibility of the extraction experiments was performed at 25 ^{0}C. In these experiments the solvent to oil ratio were three The results are summarized in Table (3) and Figure. (4).

Table 3. Reproducibility of extraction Initial concentration of 0.17wt%, mixing speed of 300rpm, time=3 hrs

	Yield Vol %	SWt %	Yield Vol%	SWt%	Yield Vol%	Swt%
1	97	0.076	98	0.0570	90	0.03310
2	98	0.076	99	0.0571	90.5	0.03321
3	98	0.075	99	0.0569	90.5	0.03281
4	98	0.077	99	0.0571	90	0.03347

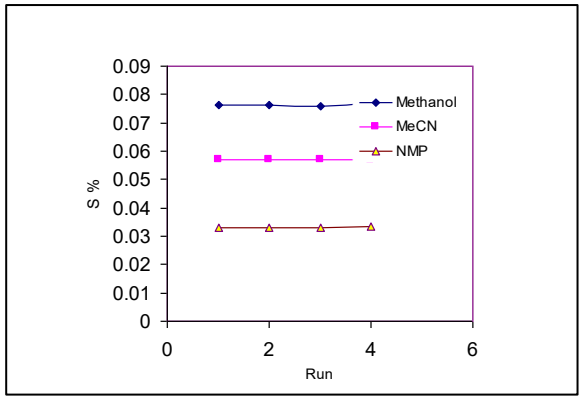


Figure. 4 Extraction experiment reproducibility

3. Results and Discussions

Extraction of DBT with different solvents:

One equilibrium stage and multistage solvent extraction procedure were applied to diesel fuel using three different solvents, namely methanol, acetonitrile and n-methyl-2-Pyrolidone (NMP). Sulfur model compounds dibenzothiophene (DBT) and dibenzothiophene sulfone (DBTS), were added to the sulfur free reference diesel fuel. The later was used in order to simulate oxidized diesel fuel as it is considered the oxidation product. A mixture of DBT and DBTS was tested since DBT in the oxidation procedure not completely removed.

Different parameters were studied in this research. These parameters are solvent to oil ratio, mixing speed, temperature and time. The partition coefficient KP was calculated based on extraction results obtained in this work as follow:

$$KP = \frac{Concentration\ of\ sulfur\ in\ raffinate\ layer}{Concentration\ of\ sulfur\ in\ extract\ layer}$$

The constant KP is termed the distribution or partition coefficient

Extraction of DBT with methanol at 25°C and 40^0C:

Measurements of the sulfur extraction compound DBT from the reference diesel fuel was conducted at temperatures of 25°C and 40°C, mixing speed of 300 rpm and for sulfur initial concentration of 0.17 wt %.

Tests were carried out at two extraction times 3 and 6 hours.

Desulfurization achieved was 60 %, as given in the sulfur content of the raffinate layer, at 25°C and 70 % at 40°C respectively and with oil yield of 90% by volume.

Table 4. Extraction of DBT with methanol at 25°C, mixing speed of 300rpm, initial sulfur concentration of 0.17 wt % for time of 3 hrs

Methanol/ oil ratio	Oil layer		Partition Coefficient (KP)	Methanol layer Sulfur wt %
	Yield vol. %	Sulfur wt %		
1	100	0.1410	1.95	0.072
2	99	0.098	1.5	0.062
3	97	0.076	1.61	0.047
5	90	0.064	1.52	0.042

Table 5. Extraction of DBT with methanol at 25°C, mixing speed of 300rpm, initial sulfur concentration of 0.17 wt % for time of 6 hrs

Methanol /oil ratio	Oil layer		Partition Coefficient (KP)	Methanol layer Sulfur wt %
	Yield Vol. %	Sulfur wt %		
1	99.5	0.135	2.07	0.065
2	99	0.0953	1	0.084
3	93.3	0.070	1	0.07
5	90	0.060	0.96	0.064

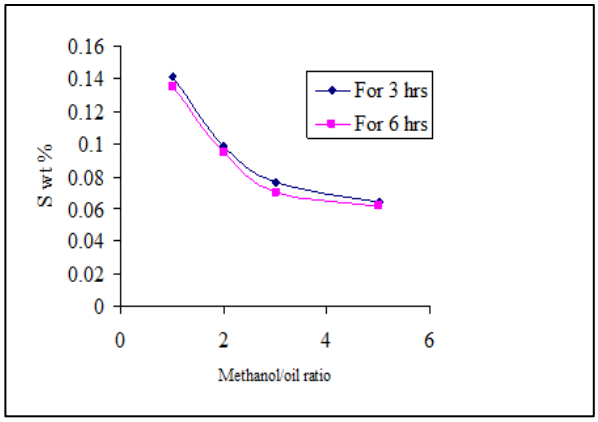


Figure. 5. Effect of extraction time of DBT with methanol at 25°c, mixing speed of 300rpm, initial sulfur concentration of 0.17 wt %

Table 6. Extraction of DBT with methanol at 40°C, mixing speed of 300rpm, initial sulfur concentration of 0.17 wt % for time of 3 hrs

Methanol/ oil ratio	Oil layer		Partition Coefficient (KP)	Methanol layer sulfur wt %
	Yield Vol. %	Sulfur wt %		
1	99.5	0.137	1.87	0.073
2	99	0.092	1.76	0.052
3	93.3	0.067	1.48	0.045
5	90	0.055	1.375	0.040

Table 7. Extraction of DBT with methanol at 40°C, mixing speed of 300rpm, initial sulfur concentration of 0.17 wt % for time of 6 hrs

Methanol/oil ratio	Oil layer		Partition Coefficient (KP)	Methanol layer Sulfur wt %
	Yield Vol. %	Sulfur wt %		
1	99.5	0.133	1.84	0.072
2	99	0.09	1.221	0.061
3	93	0.062	1.55	0.040
5	90	0.051	1.45	0.035

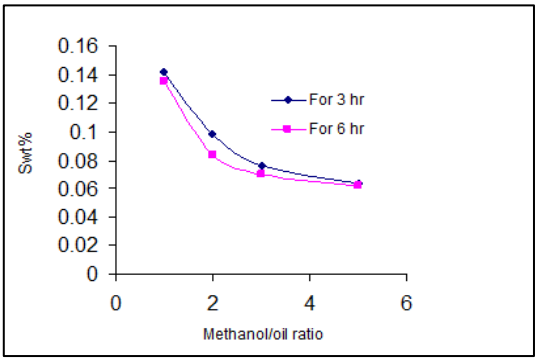


Figure. 6. Effect of extraction time of DBT with methanol at 40°c, mixing speed of 300rpm, initial sulfur concentration of 0.17 wt %

Extraction of DBT with acetonitrile at 25°C: Extraction of DBT with acetonitrile as a solvent at 25°C for extraction times of 3 and 6 hours are given in Tables (8) and (9) respectively.

Table 8. Extraction of DBT with acetonitrile at 25°C, mixing speed of 300rpm, initial sulfur concentration of 0.17 wt % for time of 3 hrs

MeCN/oil ratio	Oil layer		Partition Coefficient (KP)	MeCN Layer Sulfur wt %
	Yield Vol. %	Sulfur Wt %		
1	99.5	0.097	0.97	0.099
2	99	0.068	0.94	0.072
3	98	0.057	0.95	0.06
5	95	0.042	0.85	0.0490

Table 9. Extraction of DBT with acetonitrile at 25°C, mixing speed of 300rpm, initial sulfur concentration of 0.17 wt % for time of 6 hrs

MeCN/ oil ratio	Oil layer		Partition Coefficient (KP)	MeCN Layer Sulfur wt %
	Yield Vol. %	Sulfur Wt %		
1	99.5	0.090	0.93	0.096
2	99	0.066	0.92	0.071
3	98	0.056	0.91	0.061
5	92	0.041	0.87	0.047

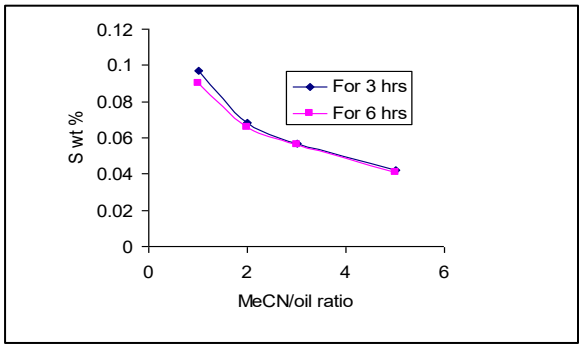


Figure. 7. Effect of extraction time of DBT with acetonitrile at 25°c, mixing speed of 300rpm, initial sulfur concentration of 0.17 wt %

Extraction of DBT with NMP at 25°C:

Extraction of DBT from the reference diesel fuel for times of 3 and 6 hours are shown in Tables (10) and (11) respectively. Deviation of extraction of DBT with NMP at 25°C and 3 hours from that at 25°C and 6 hours are less than 6%

Table 10. Extraction of DBT with NMP at 25°C, mixing speed of 300rpm, initial sulfur concentration of 0.17 wt % for time of 3 hrs

NMP/oil ratio	Oil layer		Partition Coefficient (KP)	NMP layer Sulfur wt %
	Yield Vol. %	Sulfur Wt %		
1	98	0.044	0.66	0.132
2	95	0.037	0.57	0.091
3	90	0.033	0.55	0.058
5	80	0.032	0.69	0.042

Table 11. Extraction of DBT with NMP at 25°C, mixing speed of 300rpm, initial sulfur concentration of 0.17 wt % for time 6 hrs

NMP/oil ratio	Oil layer		Partition Coefficient (KP)	NMP layer Sulfur wt %
	Yield Vol. %	Sulfur Wt %		
1	97	0.043	0.32	0.066
2	95	0.035	0.38	0.064
3	90	0.032	0.4	0.06
5	80	0.030	0.71	0.046

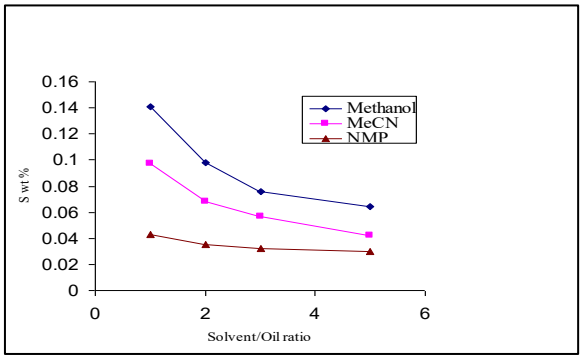


Figure. 8. Effect of extraction time of DBT with NMP at 25°c, mixing speed of 300rpm, initial sulfur concentration of 0.17 wt %

Comparison of various solvents efficiencies in extracting DBT from reference diesel fuel:

Extraction of DBT with the three solvents; namely methanol, acetonitrile and NMP for 3 and 6 hours at 25°C are given in Figures (9) and (10).

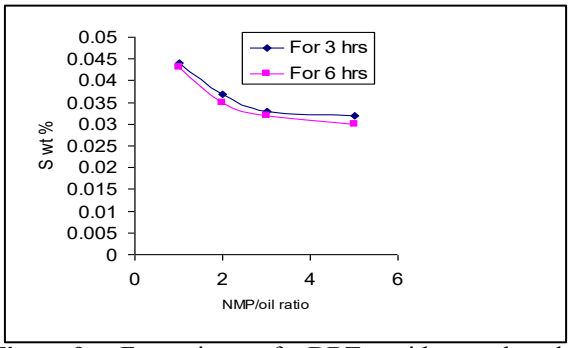


Figure.9. Extraction of DBT with methanol, acetonitrile and NMP at 25°c, mixing speed of 300rpm, initial sulfur concentration of 0.17 wt %, for time of 3 hrs

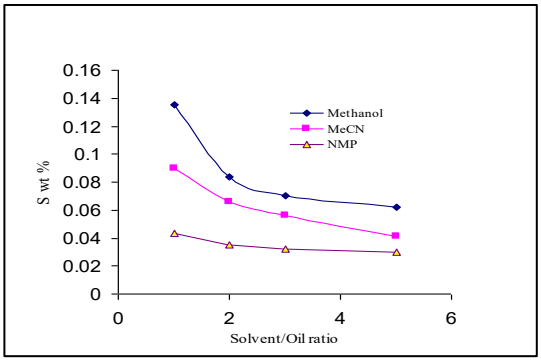


Figure.10. Extraction of DBT with methanol, acetonitrile and NMP at 25°c, mixing speed of 300rpm, initial sulfur concentration of 0.17 wt %, for time of 6 hrs

It can be seen from Figures (9) and (10) that the sulfur content of the raffinate oil layer is substantially reduced. Sulfur removal efficiencies up to 64.7 %, 76 % and 82.2 % when methanol, acetonitrile and NMP are used respectively.

4.Conclusions:

As given in the sulfur (DBT) content of the raffinate layer, desulfurization achieved when methanol is used as a solvent was 60 % at 25 °C and 70 % at 40°C respectively. Oil yield was 90 % by volume for both temperatures.

Comparison of extraction of DBT from the reference diesel fuel using acetonitrile at 3 and 6 hours gave practically similar results with absolute error less than 3 % except for the case of acetonitrile to oil ratio of one it was 7 %.

N- methyl -2- pyrolidone (NMP) is very effective solvent with a removal efficiency approaching 90 % (DBT) compared with the other solvents.

Sulfur removal efficiencies were up to 64.7 %, 76 % and 82.2 % when methanol, acetonitrile and NMP are used respectively. NMP has also been shown as the solvent that give the highest removal efficiency when DBTs and a mixture of DBT and DBTs are extracted with efficiencies of 76 % and 90 % respectively.

Solvent effectiveness factors were 6.5, 9.5 and 4.1 when methanol, acetonitrile and NMP are used respectively with solvent to oil ratio of five for extracting DBT. Based on this, it can be concluded that acetonitrile is the best solvent for extracting DBT from diesel fuels. For extracting DBTs methanol was the most effective, however, when a mixture of DBT and DBTs is extracted from the diesel fuel, acetonitrile was found as the most effective solvent with an effectiveness factor of 12.54 at a solvent to oil ratio of five.

5. Recommendations:

The use of innovative extraction agents such as ionic liquids is suggested.

Measurements of multistage extraction for a mixture of DBT and DBTs with acetonitrile is highly suggested as this solvent was shown to be the most effective and for this mixture which represent a real oxidative desulfurization process.

Extension of the prediction procedure to dibenzothiophene sulfone (DBTS) is recommended and this will require insertion of DBTS characterization data, currently not existing, into simulation packages such HYSYS.

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