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Graphical Abstract

Extraction of sulfur and polyaromatic impurities from straight run gas oil studied using performance factor combining sulfur removal and yield.
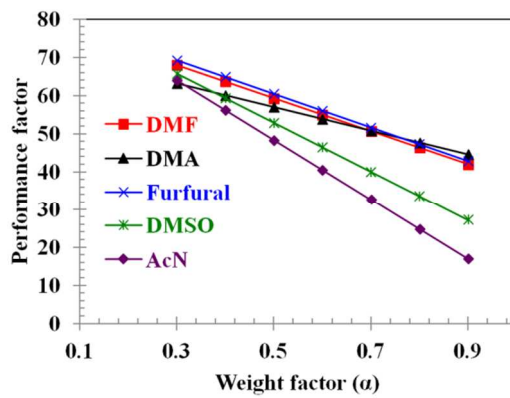
REMOVAL OF REFRACTIVE SULFUR AND AROMATIC COMPOUNDS FROM STRAIGHT RUN GAS OIL USING SOLVENT EXTRACTION

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ABSTRACT

In the present study, extraction of sulfur and polyaromatic impurities from actual straight run gas oil (SRGO) containing 1.3 wt% sulfur was studied using various solvents such as acetonitrile, N-N-dimethyl formamide, furfural, N-N-dimethyl acetamide and dimethyl sulfoxide. Effects of water as antisolvent, extraction conditions and type of extraction operation (batch, single and multi-stage and continuous) have been studied. Performance of solvent extraction process, which is governed by degree of sulfur removal (D_{sr}) and yield of extracted SRGO (ESRGO), has been evaluated in terms of a performance factor ($P_{f,\alpha}$) which has been defined in terms of weight factor ($0 < \alpha < 1$) as: $P_{f,\alpha} = \alpha D_{sr} + (1-\alpha)$yield. DMF solvent was found to be better solvent in terms of $P_{f,\alpha}$ and regeneration ability. Possibility of utilization of extract as carbon black feed stock (CBFS) has also been discussed based upon the calculated bureau of mines correlation index (BMCI) values.

Keywords: Solvent extraction; desulfurization; gas oil; performance factor; extract utilization.

INTRODUCTION

Gas oil is one of the most consumable transportation fuels and contributes significant harmful emission of NOx, SOx, HC and PM to environment. This leads to serious environmental

and health concerns such as smog, global warming and water pollution acid rain, cancer, neurotoxicity, etc.[1-5] The quantity of these emissions strongly depends on concentration of sulfur, nitrogen and aromatic compounds in gas oil used.[5] Environmental regulations have been implemented across the globe to limit the sulfur and aromatic content of gas oil for improving the air quality.[6,7]

Currently, refining industry is facing a serious challenge of meeting the increasing demand of gas oil with required stringent specifications. This challenge shall become more serious in future due to necessity of processing the sour and heavy crudes due to their increased availability. Hydrotreating is the most developed and commonly used process in the refinery for removing the sulfur and aromatic compounds from gas oil.

The cost of clean gas oil production from sour crude using conventional hydrotreatment method is increasing become drastic due to the requirement of sever operating conditions, more amount of hydrogen, noble metal based very active and expensive catalyst and huge revamp and capital depreciation cost. Refiners are looking forward to adopt the methodology to reduce the production cost of clean diesel to address the challenge of depleting profit margin in the refining. Selective solvent extraction seems an economic solution to convert high straight run gas oil (SRGO) to remove maximum amount of refractive sulfur before further treating it by conventional hydrotreating method thereby reducing the sulfur removal load and the cost of hydro treating or other alternative methods.

There are various other sulfur and aromatic removal methods such extractive, oxidative-extractive, adsorptive, oxidative-adsorptive which can be used either as a standalone or as a complementary with hydrotreating to produce ultra clean gas oil with from straight run gas oil

economically. Desulfurization using ionic liquids is widely being researched all over the world.[8-9]

Extraction with selective solvent is well proven and widely adapted processes in modern refining industries for production/removal of aromatic hydrocarbons from various hydrocarbon streams.[5,10] There are some studies which reported the removal of sulfur and heteroatomic sulfur and nitrogen compounds from gas oil boiling range hydrocarbon stream using the selective solvent extraction process.[11-18] These studies evaluated the performance of various solvents for sulfur and aromatics removal from gas oil using the single stage and multiple stage batch extraction system. However, as to our knowledge no studies are reported on continuous counter current extraction column to evaluate the performance of solvent. Similarly, of anti-solvent like water in sulfur extraction process is reported in very few studies only.[14,15] Extraction process is a trade-off between the degree of sulfur removal (D_{sr}) and yield of extracted SRGO (ESRGO). No study is reported in the literature to the best of authors' knowledge where performance of extraction process has been studied in term of a factor which combines both D_{sr} and yield.

Considering above discussion, the present study includes the evaluation of performance of industrially proven and viable solvents for removal of sulfur compounds from SRGO containing high sulfur content (1.3 wt.%). Effect of extraction temperature, solvent to feed ratio, anti-solvent concentration and number of stages (during batch operation) on the degree of sulfur and aromatics removal and yield were evaluated in batch and continuous counter current extraction system. A strategy on reutilization of the extract from industrial point of view has also been suggested.

THEORY

Liquid-liquid solvent extraction is based on the principle of difference in the solubility of solute compounds in a solvent. Degree of solubility of solutes in solvent depends upon their chemical nature. Solvent extraction process involves removal of impurities via scrubbing the hydrocarbon stream by solvent and recovery of solvent of from the scrubbed impurities for its reuse. The major challenge in the solvent extraction is to tackle the problem of desired hydrocarbon loss with the removed impurities. This loss depends on the capacity and selectivity of solvent which can be adjusted by addition of co/anti solvent and changing the extraction temperature.

A number of solvents have been reported for extraction of sulfur and aromatic compounds from gas oil oil.[11-18] However, from techno-economic view points, selection of solvent depend upon physico-chemical characteristics of solvent and feedstock, e.g. boiling point/boiling range, density, viscosity, melting point, miscibility, capacity and selectivity of solvent. The desirable features for extraction solvent have been summarized in literature.[19-24]

Physical properties can be used as preliminary tool to screen the solvents e.g. 1) sufficient density difference between solvent and feed for allowing two phase formation and avoiding the flooding in the extraction; 2) sufficient boiling point difference between solvent and feed to facilitates easy recovery of solvent for its reuse; 3) high thermal and chemical stability to avoid loss of solvent due to degradation; 4) low melting point to evade the requirement of steam tracing; 5) low viscosity for high rate of mass transfer; 6) no zoetrope formation with components in feed to facilitate the ease recovery; 7) non-toxicity for safe operation; and 8) noncorrosive to reduce capital investment. Moreover, selected solvent should further be evaluated for their high capacity for solutes to reduce the required solvent to feed (S/F) ratio and high selectivity to reduce the height of extractor and improving the quality of extract and to

increase yield of raffinate. The capacity and selectivity of solvent can be adjusted by changing the quantity of co- and anti-solvent in the main solvent and the extraction temperature.

Usefulness of a solvent in liquid-liquid extraction can be represented by extraction factor for sulfur, sulfur distribution coefficient, yield of extracted gas oil, degree of sulfur removal, and performance factor.

Extraction factor is used to represent the capacity of solvent. Extraction factor (ε_s) for single stage solvent extraction is defined as. [25]

$$\varepsilon_s = \frac{\text{Quantity of component i in the extract phase}}{\text{Quantity of component i in the raffinate phase}} \tag{1}$$

The distribution coefficient of solute (K_s) is the ratio of composition for solute in the extract phase to that in the raffinate phase and is defined as:

$$K_s = y_S / x_S \tag{2}$$

Where, y_s and x_s denote the concentration of sulfur (g/g) in the extract and in the raffinate phase, respectively. Yield of extracted straight run gas oil (ESRGO) is defined as:

$$\text{Yield}(\%) = \frac{\text{Volume of solvent free ESRGO}}{\text{Volume of SRGO}} \times 100 \tag{3}$$

The capacity of a solvent is a measure of its ability to dissolve the hydrocarbon. Considering this, volumetric yield of ESRGO can also be used to represent the capacity of solvent.

Material and component balance equations which are required to estimate the unknown value of variable in raffinate/extract phase are defined as:

$$F = R + E \tag{4}$$

$$x_{f,i} F = x_{r,i} R + x_{e,i} E \tag{5}$$

Where, F, R and E are mass of feed, raffinate and extract, respectively. $x_{f,i}$, $x_{r,i}$, and $x_{e,i}$ are respective mass fraction of component i in feed, raffinae and extract, respectively.

Degree of sulfur removal (D_{sr}) shown in the study was estimated using the following expression:

$$D_{sr} = \frac{\left(S_{SRGO} - S_{ESRGO}\right)}{S_{SRGO}} \times 100 \qquad (6)$$

Where, S_{SRGO} and S_{ESRGO} denote the concentration of sulfur in the SRGO and in ESRGO, respectively. Moreover, degree of aromatics removal can also be used to understand the effect of solvent extraction on the quality of extracted gas oil obtained under different operation conditions. Degree of aromatic removal (Dar) was calculated by the following expression:

$$A_{ar,i} = \frac{\left(A_{SRGO,i} - A_{ESRGO,i}\right)}{A_{SRGO,i}} \times 100 \qquad (7)$$

Where, $S_{SRGO,i}$ and $S_{ESRGO,i}$ denote the concentration of aromatics (mono, di and poly) in the SRGO and in ESRGO, respectively.

In light of reverse trend for capacity and selectivity of solvent, it can be understood that yield of ESRGO would decrease with increase in degree of removal of sulfur and aromatic compounds (solvent extraction hand book). However, from economic point of view of process, it is desirable to obtain the maximum yield of ESRGO with maximum removal of sulfur and poly aromatic compounds. To combine the effect of these two important parameters in single factor, performance factor (P_f) of solvent is defined as:

$$P_{f,\alpha} = \alpha D_{sr} + \left(1-\alpha\right) \times Yield(\%) \qquad (8)$$

Where, α denotes the weight factor assigned to the degree of sulfur removal.

EXPERIMENTAL

Materials

Straight run gas oil (SRGO) was obtained from an Indian refinery. Physicochemical properties of SRGO are given in Table 1. Acetonitrile (AcN: 99.5%+: MERCK), N-N-dimethyl formamide (DMF: 99.5%, MERCK), furfural (FF: 98%: SD Fines), N-N-dimethyl acetamide (DMA: 99.5%+: MERCK) and dimethyl sulfoxide (DMSO: 99.8%: MERCK) were used as extraction solvents. All compounds mentioned above were used without any pretreatment except furfural. Furfural was distilled before being used as a solvent.

Methods of analysis

Density was determined using an apparatus manufactured from Metller Toledo Japan DE45 densitometer at temperature of 20°C. Refractive index was determined using Abbe Refractometer RE45 at 20°C. Total sulfur content of the gas oil and extracted straight run gas oil (ESRGO) were estimated by X-ray fluorescence (XRF) method by using ASOMA ED XRF analyzer Spectro Phoenix II make. ASTM D86 method was used for determining the boiling range of gas oil. An ultraviolet (UV) spectrophotometric technique was used for estimation of mono, di and poly aromatics content of SRGO and ESRGO.

Apparatus and procedure

Single stage equilibrium extraction: A known amount of gas oil and solvent was charged in a jacketed glass mixer settler provided with a stirrer. The extraction temperature was maintained within $\pm0.5^{\circ}$C with the help of a thermostatic bath. The charge was stirred for 30 min which is sufficient for the establishment of equilibrium. After mixing, residence time of 30 min was provided to separate the oil rich raffinate phase from the solvent rich extract phase. Due to equilibrium solubility of solvent in hydrocarbon, raffinate phase was washed with water to remove the solvent. Solvent free raffinate was used for calculation of yield (as defined earlier).

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The moisture of the solvent free raffinate was removed using the solid ammonium sulphate. Thereafter it was analyzed for its sulfur and aromatics concentration.

Continuous counter current extraction: Continuous counter-current extraction of gas oil was carried out in a jacketed pyrex glass column of 10 mm internal diameter. The column was filled up to 140 mm of its height with 2.3 to 3.0 mm structured cannon packing. The settling zones of 15 mm were provided at the top and bottom of the column. The feed and solvent were pumped using the metering pumps at the bottom and the top of the column, respectively. The flow rates of feed and solvent were fixed so as to get the desired solvent-to-feed ratio. In extraction runs, feed was used as dispersed phase, the interface was observed at the top of the column due to the feed being lighter. The level of interface was kept constant in the settling zone at the top of the column during the run. The temperature of column was maintained by circulating the hot water in jacket of the column. The steady state of column was confirmed by constant value of RI measured for top hydrocarbon samples time to time before collecting the sample for analysis. The gas oil raffinate phase and solvent rich extract phase were obtained from top and bottom of the column, respectively. The raffinate phase was further treated in the same way as in single stage equilibrium experiments.

RESULTS AND DISCUSSION

Batch equilibrium extraction

Evaluation of solvents with SRGO: The extraction of actual SRGO was carried out using the industrially viable polar solvents such as AcN, DMF, furfural, DMA and DMSO with volumetric gas oil to solvent ratio of 1 at 45°C using procedure as described in section 3.3.1. The yields of ESRGO and degree of sulfur removal (D_{sr}) were estimated using the equations 3 and 6, respectively. Refractive Index (RI) value of aromatic compounds is higher than the paraffinic

materials. The lower value of RI of ESRGO indicates the higher removal of aromatics compounds.

The results (Table 3) clearly indicate that sulfur removal and yield of ESRGO using solvent extraction strongly depend on the type of solvent used. Percent sulfur removal using the DMF, DMA and furfural solvents are much higher than AcN and DMSO. Among the DMF, DMA and furfural, DMA removes the maximum sulfur. However, yield values for DMF, DMA and furfural solvents are lower than AcN and DMSO. It indicates that there is a tradeoff between sulfur removal and yield value. From the process's economic point of view, maximum sulfur removal with maximum yield value is desirable.

Considering this, the performance factor (P_f) for each solvent was estimated using the equation 8 using weight factor (α)=0.5, thus giving equal importance to yield and D_{sr}. The values of P_f are given in Table 3. It is observed that when the sulfur removal and yield were assigned the same value of α, values of P_f follow the order: furfural > DMF > DMA > DMSO > AcN.

The extraction factor and distribution coefficient follow the order: DMA> DMF > furfural > DMSO > AcN. However, the values of extraction factor for DMF and furfural are comparable whereas for distribution coefficient there is significant difference. It may be attributed to the difference in density of solvents.

The effect of the value of α (in the range of 0.3-0.9) on the P_f value for each solvent is shown in Figure 1. It is clear that P_f values for DMF and furfural solvents are very close to each other and that they decrease over the whole range of α. For AcN and DMSO, values of P_f are always much less as compared to other solvents at all values of α. P_f values of DMF are higher than that of DMA for $\alpha < 0.7$, however for $\alpha \geq 0.7$, P_f values of DMA become higher than that of DMF. P_f values for furfural are slightly higher than that of DMF, however, its values become

lower than that of DMA for $\alpha \geq 0.8$. Overall DMF, furfural and DMA seem to be comparable solvents in terms of P_f for whole range of α.

However, considering the low oxidative and thermal stability of furfural as reported in literature[5], lower values of extraction factor and distribution coefficient, DMF and DMA were selected as solvents for further study.

Effect of extraction temperature and water concentration: It is well known that extraction temperature affects the capacity and selectivity of any solvent. The results for experiments with varying temperatures (with no water in solvent) have been summarized in Figure 2. It may be noted that during SRGO extraction with DMA solvent, single phase formation was observed when the temperature was increased to 75 °C, therefore, experiments were carried out in the range of 45 to 65 °C for DMA and in the range of 45 to 75 °C for DMF. It is clear in Figure 2 that an increase in the extraction temperature increases the degree of sulfur removal, however, it simultaneously decrease the ESRGO yield. Therefore, $P_{f,0.5}$ seems to be unaffected by variation of temperature. However, $P_{f,0.7}$ increases with an increase in temperature and that $P_{f,0.3}$ decreases with an increase in temperature.

Water behaves as an antisolvent in extraction process as it decreases the solubility of hydrocarbon in solvent. Concentration of antisolvent in main solvent can change the performance of solvent.[15] Considering this, extraction of SRGO with DMF and DMA solvents was carried out by varying the water content in the range of 0-3.0 volume% at 65 ˚C so as to understand their impact on D_{sr} and P_f of DMF and DMA. Results are shown in Figure 3. As expected, an increase in water concentration in the solvent, increased the ESRGO yield, however, it also decreased the degree of sulfur removal for both the solvents. However, the

spread of change in $P_{f,0.5}$ for DMA solvent was marginally higher than that of DMA with increasing water concentration in solvent.

The P_f values of DMA solvent are lower than that of DMF over whole range of temperature and water concentration studied. It can be inferred that when degree of sulfur removal is more important than yield, it is better to do the extraction at higher temperature and lower water concentration and vice versa.

It may noted that P_f values for DMF are higher than the DMA values for $\alpha \leq 0.7$. Considering the significance of ESRGO yield and degree of sulfur removal in economics of extraction process, DMF can be considered as more efficient than DMA. Also, the boiling points of DMF and DMA are 153 and 165°C, respectively. Therefore, it is easier to recover the DMF from the extract using distillation. Overall, considering all the above points, DMF can be considered as better solvent than DMA, and therefore, it was selected for further studies.

Effect of solvent to feed ratio (S/F): In this study, SRGO was extracted with DMF solvent at the temperature of 65 ˚C and with volumetric solvent to feed ratio of 1.0, 1.5, 2.0, and 3.0 using single stage equilibrium extractor. The results are shown in Figure 4. It is observed that sulfur removal increased with an increase the solvent to feed ratio, whereas, the ESRGO yield decreased. $P_{f,0.5}$ values are nearly constant up to solvent to feed ratio of 2.0, however, it decreases with an increase in solvent to feed ratio beyond 2. It is important to note that energy and capital requirement of the extraction process also increase with an increase in solvent to feed ratio. Hence, solvent to feed ratio of 1.0 seems to be better for continuous extraction.

Multistage stage extraction: To understand the importance of number of equilibrium stage to meet the desired amount of sulfur removal, multistage stage solvent extraction of SRGO was carried out with DMF solvent at volumetric S/F ratio of 1.0 and extraction temperature of 65˚C.

ESRGO from 1st stage was used as feed for 2nd stage solvent extraction and that from second stage was used as feed in the 3rd stage solvent extraction. The volume of ESRGO obtained in each stage was used to estimate the yield value. Cumulative yield was also estimated for second and third stage. The sample of extracted oil in each stage was analyzed for sulfur content. The results obtained for all three stage extractions are given in Table 3. It is observed that sulfur removal decreases appreciably in 2nd and 3rd stage, whereas stage wise volumetric yield increases slightly in subsequent extraction stages. However, the cumulative sulfur removal increases radically at the cost of significant loss in cumulative yield. Cumulative sulfur removal and yield were estimated using the sulfur and volume of SRGO. This implies that it is possible to increase the degree of sulfur removal at the expense of lower yield value of ESRGO using multistage solvent extraction. The performance factor (depending upon the value of α) of subsequent stage is lower than the previous one. It seems possible to reduce the feed sulfur from 1.3% to 0.36% using the three equilibrium stage which is equivalent to 72.3% sulfur removal.

Continuous counter current extraction

ESRGO product: Continuous counter current extraction of SRGO with DMF as described in experimental section was carried out at different operating conditions by varying the temperature from 55 °C to 45°C and water concentration in solvent from 0.0 to 5.0%. Four cases were formed by selecting the two values for each temperature and water concentrations in solvent. The analysis of ESRGO obtained for these four cases, one batch extraction case and SRGO has been summarized in Table 4. The code of different runs along with experimental conditions is also given in Table 4. Sulfur, di-aromatics and poly-aromatics are major impurities in gas oil which need to be removed to produce the clean gas oil. Therefore, degrees of removal of these parameters along with degree of sulfur removal are shown in Figure 5.

It may be seen in Table 4 and Figure 5 that the percent removal of these impurities is drastically higher in continuous extraction than batch extraction. It is attributed to availability of more than one equilibrium stage in the column and increased concentration gradient across counter current extraction column. Degree of removal of these impurities increased and that the yield of ESRGO increased with an increase in temperature and decrease in water content in solvent. The removal of undesired compounds followed the order: poly-aromatics > di-aromatic > sulfur > mono-aromatics. Removal of these compounds (which have very low cetane number) would increase the cetane value of ESRGO significantly.

It will also facilitate the easier deep desulfurization of gas oil in hydrotreater under less sever operating conditions due to removal of refractive sulfur compounds and poly-aromatics responsible for slowing down of the hydrotreating reaction.[26]

Results imply that maximum extraction temperature and zero percent water concentration are desired for maximum removal of these impurities. However, yield of valuable ESRGO decreases with increased temperature and decreased water content.

P_f values for each case were estimated with the different α values to understand the overall impact of extraction temperature and water concentration on solvent extraction process. The results are shown in Figure 6. It may be seen that the $P_{f,\alpha}$ value is significantly higher for the continuous extraction process in comparison to batch extraction irrespective of the value of α. For C-ESRGO-55T-0W case (extraction temperature=55 and zero water content), the spread in P_f values is least as the sulfur removal and yield number are close to each other. It may clearly be seen that decrease in the extraction temperature spreads the P_f values i.e. there is large variation in P_f values for various α values ($P_{f,0.3}$=68.7 to $P_{f,0.7}$=74.1). Similarly, an increase in water content increases the spread of P_f values. For C-ESRGO-45T-3W case (extraction

temperature=45 and water content=3 vol%), $P_{f,0.3}$ and $P_{f,0.7}$ values were 60.4 and 74.2, respectively. Further increase in water content for C-ESRGO-45T-5W case further increased the spread of the P_f values ($P_{f,0.3}$=54.0 to $P_{f,0.7}$=72.7). Overall for α=0.7, there is marginal effect of variation of extraction temperature, however for α=0.5, P_f values decreases with an increase in water content and decrease in temperature.

Utilization of extract: Since percent removal of non-aromatics, mono-aromatics, di-aromatic and poly-aromatics, yield and density of raffinate were known, therefore, the composition of extract phase for all cases was estimated using mass and component balance and the results are shown in Figure 7. The concentration of non-aromatics compound which are desirable in ESRGO is decreasing in the extract with decreasing in temperature and increase in water concentration in the solvent. Considering the composition of extract, it should be taken into account that the extract should not be considered as a waste as this stream can be used either as a co-product such as carbon black feed stock (CBFS), rubber processing oil, fuel oil blending stream or as a high quality feed stock to secondary conversion processes units such as fluid catalytic cracker unit (FCCU), delayed coking unit (DCU) to covert it in light and middle distillates.

The FCC and delayed coker are the processes where carbon is rejected to meet the requirement of hydrogen in distillate products. The metal content, carbondoson carbon residue (CCR) and viscosity in extract stream obtained after continuous extraction would be very low and hydrogen to carbon (C/H) ratio would be significantly higher in comparison to vacuum residue (VR), thermal tar, lube extracts, pyrolysis tar and pitch streams which are used as feed in DCU. Therefore, blending of extract stream with the VR and pitch stream will not only increase

the yield of distillates which is inversely dependent on the CCR and proportionally dependent on C/H but also improve the quality of coke.[27]

Considering its utilization as a CBFS, bureau of mines correlation index (BMCI) value which is indication of quality of black carbon feed stock for extract products was estimated using the following correlation:[28]

$$BMCI = 473.7S_g - 456.8 + \left(48460/T_b\right) \tag{9}$$

Where, S_g is liquid specific gravity at 60 °F and T_b represents the average boiling point (K). Average boiling point is the arithmetic average of temperatures at 10% interval from 20 to 80%. Since extract is obtained from the gas oil stream, its average boiling point will be close to gas oil. Therefore, distillation data of gas oil was used to represent the average boiling point of extract stream. S_g was obtained by converting the density of extract stream from 20 °C to 15.5 °C and then density at 15.5 °C to specific gravity using the petroleum measurement tables.[29]

The values of estimated BMCI values along with the estimated S_g of extract streams are tabulated in Table 5. Results indicates that BMCI value increases with decrease in extraction temperature and increase in water content in solvent as selectivity of solvent for aromatic increases with respect to increase in paraffins compound (Fig. 7). As we know higher the BMCI, better the quality of CBFS, the solvent extraction should be carried out with solvent containing significant amount of water. However, the increasing trend of density of extract stream with decrease in temperature and water content also suggest decrease in C/H ratio of extract. Therefore, there is an opportunity to adjust the operating conditions of the extraction unit considering the requirement of further downstream operation to be used for raffinate and extract stream processing. For example, temperature and S/F can adjusted to higher side with zero percent water in solvent to maximize recovery of sulfur compounds to debottleneck the hydro-

treating unit to be used for raffinate processing to bring the sulfur to ppm level. Whereas, the water content can be increased to increase the aromatic concentration in extract streams so that it can be used as a CBFS feed-stock and to increase the yield of ESRGO. Overall, operating conditions of extraction is to be adjusted depending up on the further process/application to be considered for extract and raffinate streams. It may be mentioned that the BMCI values obtained for the extracts are in the range for CBFS which are being marketed by various refineries in India.[29,30]

CONCLUSIONS

Based on the results presented in the study, N-N-dimethyl formamide (DMF) solvent seems to be the best solvent for selective solvent extraction among the five most widely used solvents in hydrocarbon industries. Degree of sulfur removal compound greatly depends on the nature of solvent and operating conditions used during the extraction. Water concentration in solvent changes the value of ESRGO yield and impurities removal significantly. Extraction temperature and water content in solvent gives the flexibility to adjust the yield and degree of removal of impurities to maximize the benefit in a given situation. Continuous counter current extraction is much more effective than the single stage extraction. 71.5 % sulfur can be removed from SRGO using continuous counter current extraction at reasonable ESRGO yield. Selection of weight factor for sulfur removal and yield affects the performance factor of extraction process and need utmost care in its value selection. There is a great possibility of utilization of extract as carbon black feed stock (CBFS) as shown by comparison of the calculated bureau of mines correlation index (BMCI) values which is similar to those CBFS which are already being sold in the market.

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Table 1. Physico-chemical properties of straight run gas oil (SRGO).

Parameter	Value
Total sulfur (wt %)	1.3
Non aromatics	66.8
Mono-aromatics	18.8
Di-aromatics	8.2
Poly-aromatics	6.2
Refractive Index nd20	1.4762
Density at 20 ˚C (kg/m3)	853.24
Kinematic viscosity at 70˚ C (cst)	2.17
Kinematic viscosity at 100˚ C (cst)	1.44

ASTM D-86	
Volume%	Temperature,˚C
IBP	222.1
5	244.5
10	251.2
20	259.5
30	266.8
40	276.1
50	287.2
60	300.3
70	315
80	332.1
90	351.8
95	369.7
FBP	380.9
Distillate	97.0
Residue	2.5
Lighter	0.5

Table 2. Straight run gas oil extraction with selected solvents at 45 ˚C, S/F=1.0 and α=0.5.

	ACN	DMF	DMA	Furfural	DMSO
Raffinate properties					
Refractive index@20 °C	1.469	1.4635	1.4623	1.4657	1.4701
Density@20°, g/ml	0.84304	0.83521	0.83280	0.83468	0.84255
Sulfur in ESRGO (%)	1.18	0.81	0.76	0.8	1.03
Calculate responses					
Gas oil Yield %	87.5	81	72.5	82.5	88.5
Extraction factor	0.26	0.98	1.36	0.97	0.43
Distribution coefficient	0.22	0.62	0.73	0.53	0.28
Sulfur removal (%)	9.2	37.7	41.5	38.5	20.8
Performance factor	48.4	59.3	57	60.5	54.6

Table 3. Multistage solvent extraction with DMF.

Parameter	1st stage	2nd stage	3rd stage
Stage wise volume yield %	75.6	76.5	78.1
Cumulative volume yield (%)	75.6	57.8	45.2
Sulfur in ESRGO	0.74	0.53	0.36
D_{sr} (%)	43.1	28.4	32.1
Cumulative D_{sr} (%)	43.1	59.2	72.3
Performance factor (P_f)	59.3	52.4	55.1

Table 4. Analysis of feed and products obtained during batch and continuous extraction with DMF.

Parameters	SRGO	B-ESRGO-55T-0W	C-SRGO-55T-0W	C-ESRGO-45T-0W	C-ESRGO-45T-3W	C-ESRGO-45T-5W
Experimental Conditions						
Batch or Continuous		Batch	Continuous	Continuous	Continuous	Continuous
Extraction Temp. (^{o}C)	-	55	55	45	45	45
Water content (vol%)	-	0	0	0	3	5
Experimental results						
Density at 20 ˚C (g/ml)	853.24	836.60	824.10	829.03	829.80	833.95
Volume Yield (%)	-	79.1	74.3	78.1	84.5	86.7
Sulfur (wt %)	1.3	0.79	0.37	0.46	0.65	0.78
Non- aromatics (wt %)	71.3	80.9	89.4	88.4	85.6	83.5
Mono-aromatics (wt %)	16.8	12.5	8.7	8.9	9.6	10.5
Di-aromatics (wt %)	7.2	4.4	1.3	1.9	3.1	3.9
Poly-aromatics (wt %)	4.7	2.2	0.6	0.8	1.7	2.1
Performance factor (P_f)		31.0	53.2	50.5	42.3	34.7

Table 5. Properties and BMCI of extract streams.

Parameter	B-ESRGO-55-0W	C-SRGO-55-0W	C-ESRGO-45-0W	C-ESRGO-45-3W	C-ESRGO-45-5W
Density @20 °C	0.9162	0.9375	0.9396	0.9810	0.9853
Density @ 15.5° C	0.9194	0.9407	0.9428	0.9842	0.9885
Specific gravity @ 15.5	0.9199	0.9412	0.9433	0.9848	0.9891
Ave boiling point, °C	291.00	291.00	291.00	291.00	291.00
BMCI	65.2	75.3	76.3	95.9	98.0
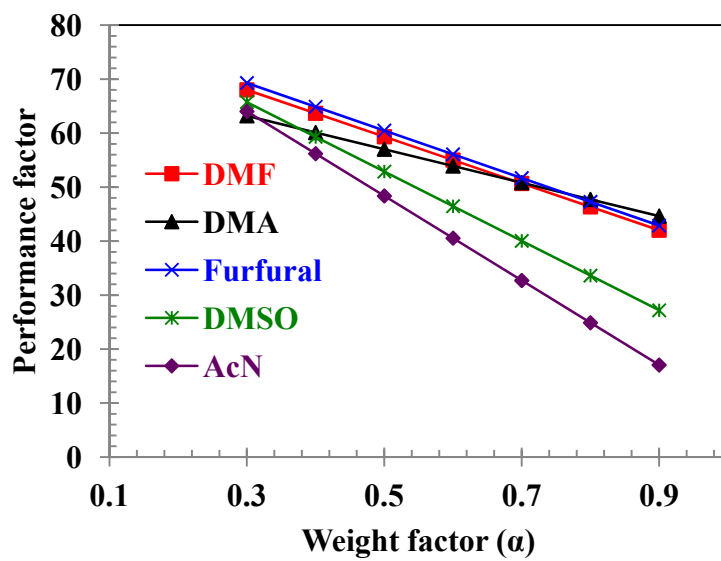
Figure 1. Effect of weight (α) on solvent's performance factor ($P_{f,\alpha}$) during extractive desulfurization of SRGO by various solvents.
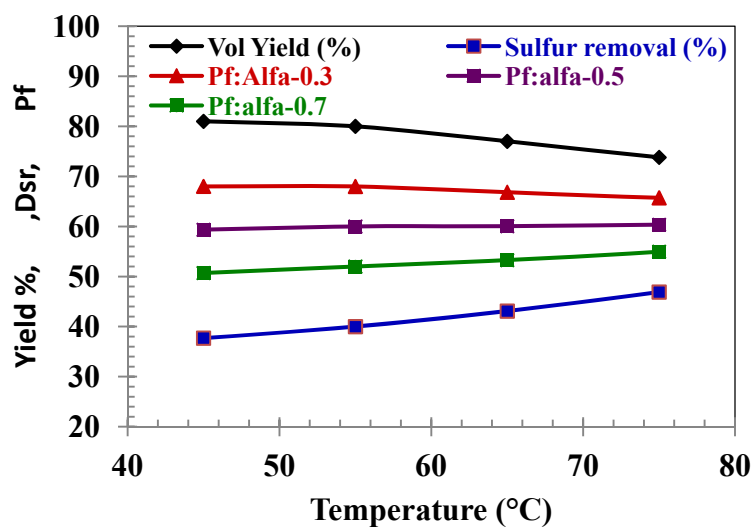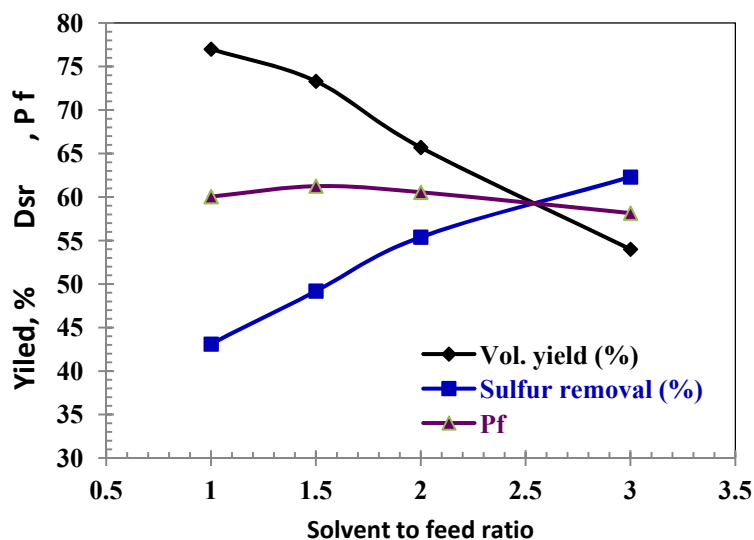
(a) DMF
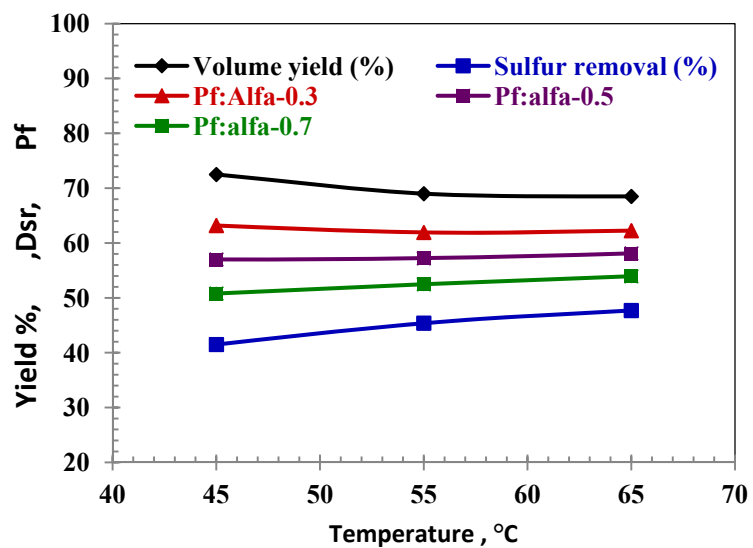
(b) DMA

Figure 2. Effect of extraction temperature on volume yield%, degree of sulfur removal (D_{sr}) and solvent's performance factor ($P_{f,\alpha}$) for solvent to feed ratio of 1.
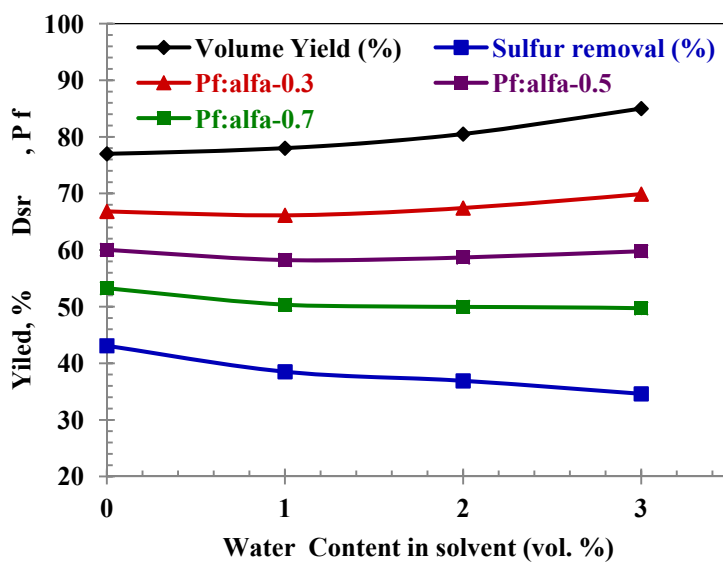
(a) DMF
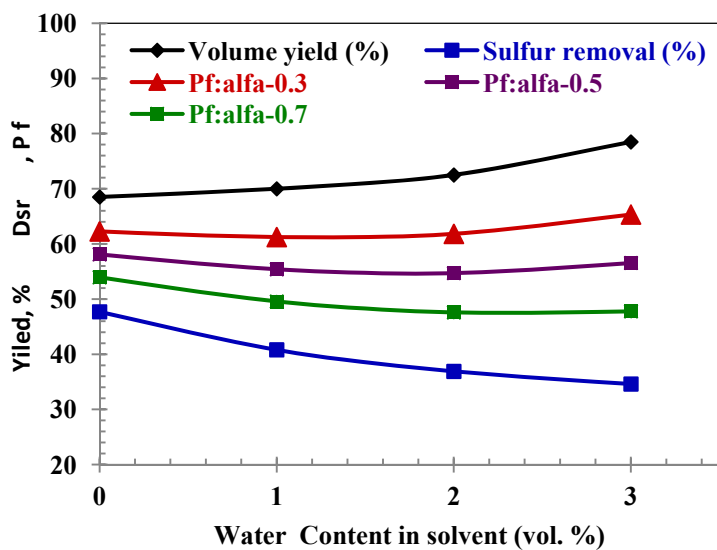
(b) DMA

Figure 3. Effect of anti-solvent (water) concentration on volume yield%, degree of sulfur removal (D$_{sr}$) and performance factor (P$_{f,\alpha}$) for solvent to feed ratio=1.0 and Temperature=65 °C.

Figure 4. Effect of solvent to feed ratio on volume yield%, degree of sulfur removal (D_{sr}) and solvent's performance factor ($P_{f,\alpha}$) for batch extraction using DMF as solvent for α=0.5 and temperature=65°C.
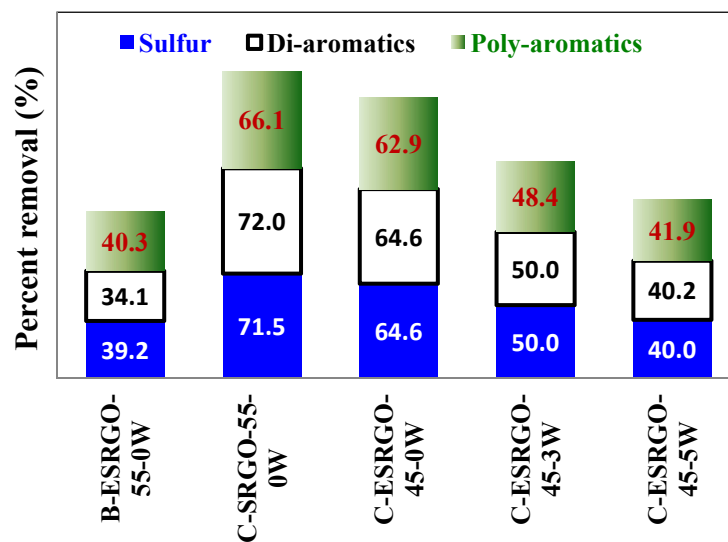
Figure 5. Comparative analysis of degree of sulfur, di-aromatics and poly-aromatics removal during batch and continuous extraction using DMF as solvent at various experimental conditions.
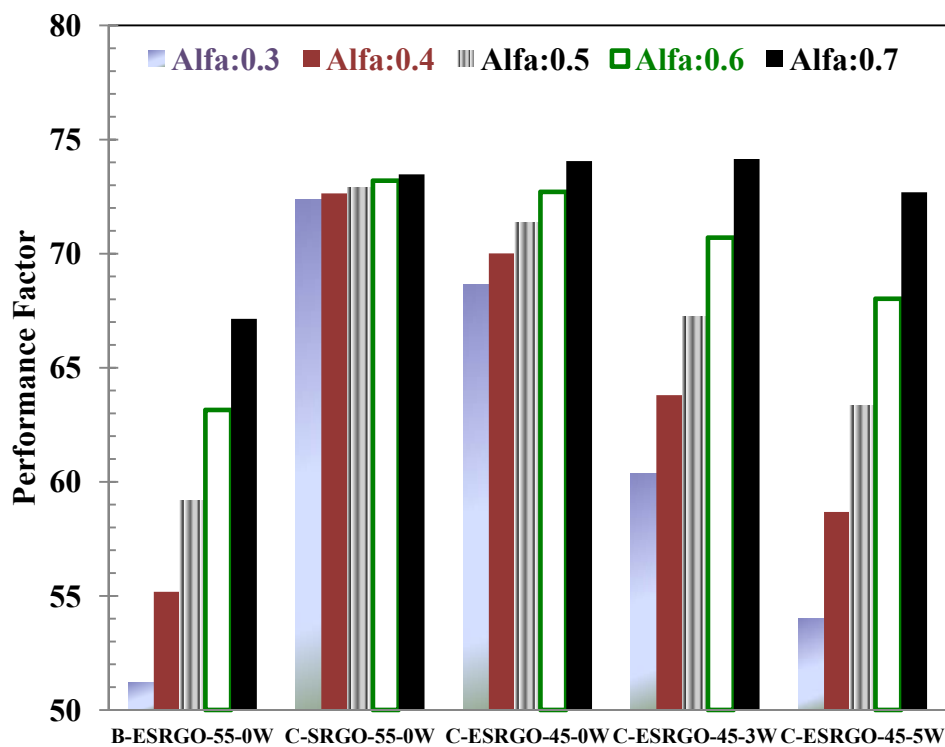
Figure 6: Effect of weight factor (α) on solvent's performance factor ($P_{f,\alpha}$) during batch and continuous extraction using DMF as solvent at various experimental conditions.
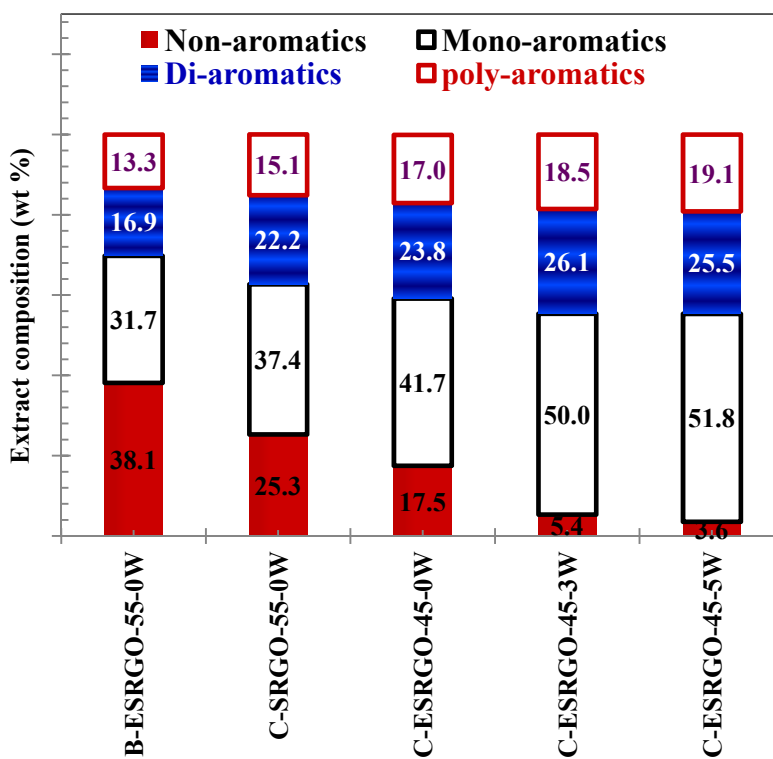
Figure 7: Composition of extract phase obtained during batch and continuous extraction using DMF as solvent at various experimental conditions.

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