STUDIES ON SOLVENT EXTRACTIVE DESULFURIZATION OF GAS OIL

Ph.D. THESIS

by

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DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
ROORKEE - 247 667 (INDIA)

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A THESIS

Submitted in partial fulfilment of the
requirements for the award of the degree

of

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in

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in this thesis entitled **"STUDIES ON SOLVENT EXTRACTIVE DESULFURIZATION OF GAS OIL"** in partial fulfilment of the requirement for the award of the Degree of Doctor of Philosophy and submitted in the Department of Chemical Engineering of the Indian Institute of Technology Roorkee is an authentic record of my own work carried out during a period from December, 2011 to June, 2015 under the supervision of Dr. V. C. Srivastava, Associate Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee and Dr. S. M. Nanoti, Chief Scientist, Refinery Technology Division, CSIR-Indian Institute of Petroleum, Dehradun.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other Institute.

(SUNIL KUMAR)

This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

(V. C. Srivastava)
Supervisor

(S. M. Nanoti)
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Date: June , 2015

ABSTRACT

Gas oil is extensively used in the transportation vehicles such as cars, buses, trucks, locomotives, marines, etc.; and static equipment such as generators, farm pumping set, engines, etc. Diesel share among transportation fuels and its demand has grown significantly over the last few years and this trend is expected to continue for the coming years due to inherent benefits, such as low market price and higher calorific value and higher engine thermal efficiency of diesel in comparison to gasoline. However, its combustion contributes significant harmful emission of nitrogen and sulfur oxides, unburnt hydrocarbons and particulate matter to the environment. This leads to serious environmental and health concerns such as smog, global warming and water pollution, acid rain, cancer, neurotoxicity, etc. [Srivastava, 2012]. Quantities of these emissions increase with an increase in concentration of sulfur, nitrogen and aromatic compounds in gas oil. Therefore, environmental regulations have been implemented across the globe to limit the sulfur and aromatic content of gas oil for improving the air quality. Thus, deep removal of sulfur and poly aromatics from gas oil is the need of the hour to minimize the emissions of oxides of sulfur, poly aromatic hydrocarbons (PAH), particulate fines, etc.; to minimize corrosion and wear of engine systems; and to improve the performance of emission control technologies.

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 crude. Hydro-treatment is the well established process for removal for sulfur and poly aromatics from gas oil in the refineries. It is known that benzothiophene (BT), dibenzothiophene (DBT) and their alkylated derivates are refractory sulfur compounds which remain in hydrotreated gas oil as well. The condensed polyaromatics in gas oil act as inhibitors during hydrotreatment of refractive sulfur compounds because of strong competition among aromatic and sulfur compounds for adsorption on catalyst active sites. Nitrogen compounds such as carbazole and acridine (dibenzo[b,e]pyridine) retard the performance of hydrotreatment even at low concentrations .

Deep removal of these impurities using hydrotreatment requires very severe operating conditions of temperature and pressure, expensive catalysts, revamp of existing hydrogen plant for capacity enhancement or installation of new H_2 generation plant so as to meet the significantly increased H_2 consumption and H_2S-free H_2 recirculation. These activities require significant increase in operating cost and huge capital investment requirement to revamp the existing facilities [Srivastava, 2012]. Therefore, in this competitive world, when refinery margin for processing a barrel of crude is decreasing, refineries are looking for optimizing the conversion and investment cost for meeting the new stringent ultra low sulfur specification in gas oil.

Various researchers are working in the area of development of non-hydrodesulfurization methods such as oxidative desulfurizataion (ODS) [Arellano et al., 2014; Yu et al., 2013; Maity et al., 2012; Bhasarkar et al., 2013], selective adsorptive desulfurization (ADS) [Nair and Tatarchuk, 2011; Shalaby et al., 2009], biodesulfurization (BDS) [Agarwal and Sharma, 2010; Mukhopadhyaya et al., 2007], and solvent extraction desulfurization (SEDS) [Rodríguez-Cabo et al., 2012] that have the potential to be used as either stand alone or as complementary method with hydrodesulfurization for cost effective production of ultra clean gas oil. Desulfurization process can be made more economical by using combination of processes. SEDS process can remove the refractive sulfur compounds, polyaromatics and nitrogen compounds to a very large extent [Gaile et al., 2010] and can be used prior to conventional hydrotreatment process for attaining the goal of deep desulfurization at lower capital and operating costs than required in standalone hydrotreatment method.

Although, solvent extraction is widely adapted process in refining industries for production/removal of aromatics, however, its application for gas oil desulfurization is in research and development stage. Some computational studies for solvent screening using the capacity, selectivity and performance index (capacity × selectivity) at infinite dilution as performance indicators for removal of model sulfur, aromatic and nitrogen compounds have been reported [Anantharaj and Banerjee, 2011a,b]. In these studies, target compounds are thiophenes, BT and DBT sulfur compounds and the solvent is ionic liquid. Removal of sulfur, aromatics and nitrogen compounds from liquid fuels using single-stage batch and multistage (set of separating funnels) continuous counter-current solvent extraction have also been reported [Gaile et al., 2010]. These studies are based on either straight run gas oil (SRGO) or hydrotreated gas oil or vacuum gas oil feed stocks. Further, either degree of sulfur removal (D_{sr}) or sulfur removal capacity and yield of gas oil have been used as solvent performance indicators.

An exhaustive literature review reveals that there are number of aspects of extractive desulfurization of gas which need to be studied for paving the path of its successful commercialization of SEDS in the refinery. Considering various possibilities, work on various aspects was carried out in the present study to bridge some research gaps and provide the insight of extractive desulfurization capabilities for desulfurization of gas oil streams.

In the first part of this work, a new strategy for a realistic and practical screening of solvents for removal of highly refractory sulfur and nitrogen compounds from gas oil has been evolved and presented. Two major class of solvents vis a vis conventional organic solvents and ILs are used for aromatic, sulfur and nitrogen compounds removal from hydrocarbon streams. Six most widely used industrially proven conventional organic solvents and twenty two imidazolium based IL solvents were selected for removal of BT, DBT and their alkylated derivatives, and nitrogen compounds from gas oil. The solubility parameters, molar volume, van der Waals volume of sulfur, aromatics and nitrogen compounds which can represent the gas oil were estimated using ab initio molecular dynamics method. These parameters were used for estimating the standard heat of vaporization and activity coefficients at infinite dilution of model gas oil compounds in solvents using available correlations. The capacity, selectivity and performance index (P_I) of solvents were estimated for selected sulfur and nitrogen compounds. To understand the effect of complexity of solvent recovery section on their industrial utilization, two type of solvent recovery sections were conceptualized for recovering of solvents: one having boiling point lower than gas oil, and the other, for solvents having boiling point in the range gas oil distillation. Based on complexity of recovery section, a new industrial usability index (S_{IUI}) of solvent was defined and used for their rating for sulfur and nitrogen compounds from gas oil. The solvents were ranked for removal of BT, DBT and their alkylated derivatives sulfur compounds, quinoline, indole and carbazole nitrogen compounds from gas oil. It was observed that selectivity and capacity values of solvents for nitrogen compounds are higher than most of the sulfur compounds. Rankings based on selectivity and capacity correlated well with the solubility parameter. It was also observed that ranking of solvents strongly depends on the parameter/index selected for the ranking. P_I which combines the effect of both capacity and selectivity seems to be better index than individual capacity and selectivity indexes to rank the solvents. Industrial usability index (S_{IUI}) of solvents which includes $\mathrm{P_I}$ and process complexity factor of solvent recovery seems more practical and realistic criteria to be used for solvents assessment for a given separation. 4,6 dimethyl DBT and quinoline WEre most refractory sulfur and nitrogen compounds to be removed among selected compounds in the study. Overall, organic solvents were found to be better solvents for desulfurization and denitrogenation of gas oil as compared to ionic liquid solvents. There was no single solvent which ranked 1st for all sulfur and nitrogen compounds removal from gas oil. Therefore, the detailed sulfur component analysis of gas oil is plays an important role in selection of solvent. Moreover, it seems that the best solvent should have moderate capacity, selectivity and lower boiling point than gas oil.

Further, experimental evaluation of industrially proven and viable organic solvents was carried out for extraction of sulfur and polyaromatics impurities from actual SRGO containing 1.3 wt% sulfur. Effect of extraction temperature, solvent to feed ratio, anti-solvent concentration and number of stages (during batch operation) on the $\mathrm{D_{sr}}$ and aromatics removal and yield were evaluated in batch and continuous counter current extraction system. Performance of a solvent extraction process which is governed by D_{sr} and yield of extracted SRGO (ESRGO) was evaluated in terms of a performance factor ($P_{f,\alpha}$) which had 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 point of views. Comparative analysis of degree of sulfur, di-aromatics and poly-aromatics removal during batch and continuous extraction using N-N-dimethyl formamide (DMF) as solvent at various experimental conditions reveal that water concentration in solvent changes the value of ESRGO yield and impurities removal significantly. Extraction temperature (T_E) 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. Selection of weight factor for sulfur removal and yield affects the performance factor of extraction process and need utmost care in its value selection.

To optimize the operating variables for continuous SEDA, a full factorial central composite design (CCD) method was used to design the experiments for extractive desulfurization of SRGO in packed bed extractor using DMF as solvent. The operational parameters namely anti-solvent water concentration (W_c) in main solvent, solvent to feed ratio (S/F), and extraction temperature (T_E) which affect the sulfur removal and yield were used as input variables in design of experiments. Considering the trade off phenomenon between sulfur removal and yield, multi-response optimization with desirability function approach was used to estimate the optimized value of these operating parameters so as to maximize sulfur removal and yield of ESRGO. Optimum values of selected variables were: water content in solvent=2.91 vol.%, solvent to feed ratio=1.70 and extraction temperature=46.4^{o}C. At the maximum desirability value, ESRGO yield and percent sulfur removal were 81.7% and 60.5%, respectively. Since, importance of sulfur removal and yield would depend on the secondary process to be selected for reducing the sulfur to 50-10 ppm, an analysis of goal importance effect on optimized value of operational parameters for maximum desirability was also studied**.**

Solvent extraction works on the principle of relative solubility of feed compounds in solvent. There are various gas oil streams which have significant different composition of paraffines, naphthenes, aromatics and sulfur compounds refinery. Therefore, to illustrate the effect of sulfur compounds molecular structure on its extractability and to understand the effect of carrier phase composition on D_{sr}, SEDS of various synthetic sulfur compounds from synthetic carrier phases of different composition was carried out using DMF as solvent. It was found that extractability of sulfur compounds strongly depends on the its nature and carrier phase composition. Moreover, DMF solvent extraction of SRGO, LCO, CGO and MGO samples (having significantly different sulfur compounds and composition) further verified that performance parameters such as yield of raffinate, D_{sr}, distribution coefficient, extraction factor and $P_{f,\alpha}$ depend on gas oil sample composition.

To understand the effect of extraction operating conditions and importance of use of water in solvent for enhancing the extractive desulfurization performance, solvent extraction SRGO, LCO, CGO and MGO was studied using industrial N-methyl-2-pyrrolidone (NMP) solvent in single stage batch extractor and continuous counter current packed bed extraction column. Effect of T_E, S/F, W_c on D_{sr}, yield of extracted gas oil (Y%) and $P_{f,\alpha}$ was studied in single stage batch extractor for SRGO, LCO and CGO. After optimizing the operating conditions for SRGO, LCO, and CGO in single stage batch extractor, studies on mixed gas oil (MGO) were carried out in single stage batch extractor and in continuous counter current packed bed at estimated optimized values of T_E, S/F and W_c. The major issues associated with solvent extraction for gas oil desulfurization are to minimize the loss of valuable hydrocarbon with extract and value addition to extract hydrocarbon. Both these issues have been addressed in the present study by generating pseudo-raffinate from the extract phase using water as antisolvent so as to minimize the loss of valuable hydrocarbon with extract and improving the quality (BMCI) of extract hydrocarbon for their utilization as CBFS in black carbon generation process. It may be mentioned that the BMCI values and sulfur content of extract hydrocarbon was found in the range for CBFS which are being marketed by refineries in India. Quantitative evaluation of distillate products from processing of the pseudo raffinate (generated from the extract phase using antisolvent) in hydrocracker and fluid catalytic cracking (FCC) processes was also carried out. The benefits and befitting of disposal of extract hydrocarbon in delayed coker as blending stream with vacuum residue (VR) was explored.

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SUNIL KUMAR

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NOMENCLATURE

ABBREVIATIONS

2,5-DMT	2,5-dimethylthiophene
4,6-DMDBT	4,6 Dimethyl-dibenzothiophene
2,3,6-TMDBT	2,3,6-trimethyl dibenzobenzothiophene
2-MT	2-methylthiophene
4-MDBT	4-dimethyldibenzothiophene
A	Aromatics
ACN	Acetonitrile
ADC	Atmospheric distillation column
ADS	Selective adsorptive desulfurization
AGO	Atmospheric gas oil
AS	Anti-solvent
B	Batch
BS	Bhart stage
BDS	Biodesulfurization
BF_4	Tetrafluoroborate
BMA	Bis(methylsulfonyl)amide
BMCI	Bureau of mines correlation index
Br	Bromide
BT	Benzothiophene
BTA	Bis-(trifluoromethylsulphonyl)amide
BTX	Benzene, Toluene and Xylene
C	Continuous
$C_4H_{10}O_2$	2-ethoxyethenol
$C_4H_6O_2$	γ-butyrolactone
CH_3SO_3	Methyl sulfate
Carba	Carbazole
CBFS	Carbon black feed stock
CCD	Central composite design

CCR	Conradson carbon residue
CF_3SO_3	Trifluoroacetate
CGO	Coker gas oil
CH_3COO	Acetate
Cl	Chloride
CLO	Commercial light oil
CN	Cetane number
COSMO-RS	Conductor like screening model along with its extension to real solvents
CP-I and CP-II	Carrier phase I and II
CS	Co- solvent
CS/F	Co- solvent to feed ratio
DAO	Deasphlated oil
DBT	Di-benzothiophene
DCU	Delayed coking unit
Dec	Decanoate
Des-GO	Desulfurized gas oil (raffinate)
DMA	N,N-dimethyl acetamide
DMAA	Dimethylacetamide
DMBT	3,5 Dimethylbenzothiophene
DMDBT	4,6 Dimethyl-dibenzothiophene
DMF	N,N dimethyl formamide
DMP	Dimethyl phosphate
DEP	Diethyl phosphate
DBP	Dibutyl phosphate
ppmw	Part per million on weight basis
DMSO	Dimethyl sulfoxide
DOC	Diesel oxidation catalyst
DP	Diesel pool
E	Extract
E- EPCE	Extract obtained from continuous extraction of MGO
Ebcd-CP	3-Ethylbicycl decane

ECD	Emission control technologies/devices
E-EPSRG	Extract obtained from extract phase of pseudo raffinate generation
EG	Ethylene glycol
EMIM	1-ethyl-3-methylimidazolium
MMIM	1-methyl-3-methylimidazolium
BMIM	1-butyl-3-methylimidazolium
CH_3COO	Acetate
$EtSO_4$	Ethyl sulphate
EMMOR	4-ethyl-4-methylmorpholium
EMPIP	1-ethyl-1-methylpiperidium
EPY	1-ethyl-1-methylprrolidium
EPYRO	1-ethyl-1-methylpyrrolidinium
ESRGO	Extracted straight run gas oil
F	Feed
FA	Furfuryl alcohol
FBP	Final boiling point
FCCU	Fluid catalytic cracker unit
Furfu	Furfural
GHG	Green house gases
GP	Gasoline pool
H_2	Hydrogen
HC	Unburnt Hydrocarbon
HCO	Heavy cycle oil
HCU	Hydrocracker unit
HCGO	Hydrocracker gas oil
HDS	Hydrodesulfurization
HR	Heavy residue
IBP	Initial boiling point
ILs	Ionic liquid solvents
Indo	Indole
LCO	Light cycle oil

LGO	Light gas oil
LPG	Liquefied petroleum gas
LR	Long residue
MBT	3-Methyl Benzothiophene
MC	Methyl Cellosolve;
MOF	Metal organic frameworks
NPT	Constant number of particles, pressure and temperature ensemble
NVT	Constant number of particles, volume and temperature ensemble
NVE	Constant number of particles, volume and energy ensemble
MDBT	4-Methyl-Dibenzothiophene
Me-Et-EtSu	2-(2-methoxyethoxy)ethyl sulfate
MGO	Mixed gas oil (mixture of SRGO, LCO and CGO)
MIM1	1-Methacryloyloxyhexyl-1-methylimidazolium Bromide
MIM10	1-Hexyl-3-methylimidazolium Hexafluorophosphate
MIM11	1-Octyl-3-methylimidazolium Hexafluorophosphate
MIM12	1-Methyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide
MIM13	1-Ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide
MIM14	1-Butyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide
MIM15	1-Methyl-3-methylimidazolium Dimethylphosphate
MIM16	1-Ethyl-3-methylimidazolium Ethylsulfate
MIM17	1-Methyl-3-methylimidazolium Methoxyethylsulfate
MIM18	1-Butyl-3-methylimidazolium Trifluoromethanesulfonate
MIM19	1-Butyl-3-methylimidazolium Diethyleneglycolmonomethylethersulfate
MIM2	1-Propyl-2,3-dimethylimidazolium Tetrafluoroborate
MIM20	1-Hexyloxymethyl-3-methyl-imidazolium Bis(trifluoromethylsulfonyl)imide
MIM21	1,3-Dihexyloxymethylimidazolium Bis(trifluoromethylsulfonyl)imide
MIM22	1-Butyl-3-methylimidazolium Octylsulfate
MIM3	1-Ethyl-3-methylimidazolium Tetrafluoroborate
MIM4	1-Butyl-3-methylimidazolium Tetrafluoroborate
MIM5	1-Hexyl-3-methylimidazolium Tetrafluoroborate
MIM6	1-Octyl-3-methylimidazolium Tetrafluoroborate

MIM7	1-Hexadecyl-3-methylimidazolium Tetrafluoroborate
MIM8	1-(2-Hydroxyethyl)-3-methylimidazolium Tetrafluoroborate
MIM9	1-Butyl-3-methylimidazolium Hexafluorophosphate
MSACN	Methylsulfonylacetamide
NMP	N-Methyl-2-pyrrolidone
Npn-A	1-n-propyl napthalene
NO_x	Nitrogen oxides
NRTL	Non-random two-liquid
NT	Nitrate
OcSu	Octylsulfate
ODS	Oxidative desulfurization
PAH	Polyaromatic hydrocarbon
PF_6	Hexafluorophosphate
PFPD	Pulsed flame photometric detector
PM	Particulate matters
PR	Pseudo raffinate
PSA	Pressure swing adsorption
Quin	Quinoline
R	Raffinate
R- EPCE	Raffinate obtained from continuous extraction of MGO
RI	Refractive Index
SC	Sulfur content
SRC	Solvent recovery column
RWC	Raffinate wash column
SCN	Thiocyanate
SEDS	Solvent extractive desulfurization
Smax	Maximum amount of solvents
Smin	Minimum amount of solvents
sp	Solvent rich phase
SRGO	Straight run gas oil
SRLGO	straight run light gas oil

SULFO	2,3,4,5-tetrahydrothiophene-1,1-dioxide (Sulfolane)
T	Thiophene
TCSF	Temperature controlled separating funnels
Ted-NP	N-tetradecane
TfO	Triflate
THFA	Tetrahydrofurfuryl alcohol
TMBT	2,3,4 trimethyl benzothiophene
TMPYZO	1,2,4-trumethylpyrazolium
UNIQUAC	UNIversal QUAsiChemical
VbGO	Visbreaker gas oil
VGO	Vacuum gas oil
VR	Vacuum residue
WWFC	World fuel charter
XRF	X-ray fluorescence
LBH	Low boiling hydrocarbon
SOF	Soluble organic fraction
SO_2	Sulfur dioxide
SEDS	Solvent extractive desulfurization
SDC	Solvent drying column
SO_x	Sulfur oxides
TH	Thiophene
4, 6, 9-TMDBT	4, 6, 9-Trimethyldibenzothiophene

NOTATIONS

C_i	Capacity of solvent for component, i
D	Overall desirability
D_{ar}	Degree of aromatic removal
D_{sr}	Degree of sulfur removal (%)
H/F	Hexane to feed ratio
k	Number of responses

K	Solvent power
K_s	Distribution coefficient of solute
L	Lower limit of operating parameters
L_i	Minimum acceptable value of response
n	Number of process parameters
$OP_{e,j}$	Estimated operating parameter for MGO with j being W_c or S/F or T_E
$OP_{i,j}$	Optimized parameters with j being W_c or S/F or T_E and i being SRGO, LCO and CGO.
P_{cf}	Process complexity factor
$P_{f,\alpha}$	Performance factor
P_I	Performance index of solvent
R	Universal gas constant (J/K/mol)
r	Weight factor and positive constant
r_{vdw}	Van der Waals volume (cm^3/mol)
S/F	Solvent to feed ratio
S_{ESRGO}	Concentration of sulfur in extracted straight run gas oil (weight %)
S_f	Concentration of sulfur in the feed
S_g	Liquid specific gravity at 60 °F
S_{ij}	Selectivity of solvent for component I with respect to j
S_{IUI}	Industrial usability index of solvent
sp	Solvent rich phase
S_r	Concentration of sulfur in the raffinate
S_{SRGO}	Concentration of sulfur in the straight run gas oil (weight %)
T_{90}	Distillation temperature corresponding to 90% vaporization of gas oil
T_b	Average boiling point (K)
T_E	Extraction temperature (°C)
U	Upper limit of operating parameters
U_f	Uncertainty factor
U_i	Maximum acceptable value of response
V_m	Molar volume (cm^3/mol)
W_c	Water concentration in main solvent (volume %)

$x_{e,i}$	Mass fraction of component i extract
$x_{f,i}$	Mass fraction of component i in feed
X_i	Coded variable
x_i	Variable
x_{imax}	Maximum value of the variable
x_{imin}	Minimum value of the variable
$x_{r,i}$	Mass fraction of component i in raffinate
x_s	Concentration of sulfur (g/g) in the raffinate phase
Y	Yield of raffinate (%)
Y_1	Yield of extracted straight run gas oil (%)
Y_2	Degree of sulfur removal (%)
Y_i	Response
y_s	Concentration of sulfur (g/g) in the extract phase
α	Weight factor assigned to the degree of sulfur removal
γ^{∞}	Activity coefficients at infinite dilution
δ	Hildebrand solubility parameter J/cm^3)$^{1/2}$
ΔE_{ced}	Cohesive energy density (J/cm$^{3)}$
ΔH_v	Enthalpy of vaporization (J/mol)
ε_s	Extraction factor

Chapter – 1

INTRODUCTION

1.1. GENERAL

Modern refineries are highly integrated industrial plants in which crude oil is processed through a range of physical and chemical processes like distillation, solvent extraction, reforming, hydrogenation, cracking, blending, etc. to produce higher valuable products. These products include liquefied petroleum gas, gasoline, kerosene, jet fuel, gas oil, wax, lubricating oil, bitumen and petrochemicals. Steam, electricity, and hydrogen are also generated for internal and external use in the refinery (Babich and Moulijn, 2002). Figure 1.1 illustrates the processing of crude oil in a refinery. It may be noted that all process shown in Figure 1.1 for crude processing may not be present in every refinery as it depends upon the type of products being produced in the refinery.

It is interesting to note that fuels accounts for 75-85% of the total refinery products. (Babich and Moulijn, 2002; Sharma et al., 2013). Among these fuels, gas oil is extensively used in the transportation vehicles such as cars, buses, trucks, locomotives, marines and static equipment such as generators, farm pumping sets and engines. Over the last few years, diesel share among transportation fuels has grown significantly and this trend is expected to continue in near future years due to inherent benefits such as low market price, higher calorific value and higher engine thermal efficiency of diesel in comparison to gasoline, (Stanislaus et al., 2010). However, combustion of diesel contributes significant harmful emissions of nitrogen and sulfur oxides, unburnt hydrocarbons, poly aromatic hydrocarbon (PAH) and particulate matter (PM) to the environment. This leads to serious environmental and health concerns such as smog, global warming, acid rain, cancer, neurotoxicity, etc. (Srivastava, 2012). Quantities of these emissions increase with an increase in concentration of sulfur, nitrogen and aromatic compounds in gas oil. Various environmental regulations have been implemented across the globe to limit the sulfur and aromatic content of gas oil for improving the air quality. Thus, deep removal of sulfur and poly aromatics from gas oil is the need of the hour to minimize the emissions of oxides of sulfur, PAH, particulate fines, etc.; to minimize corrosion and wear of engine systems; and to improve the performance of emission control technologies.

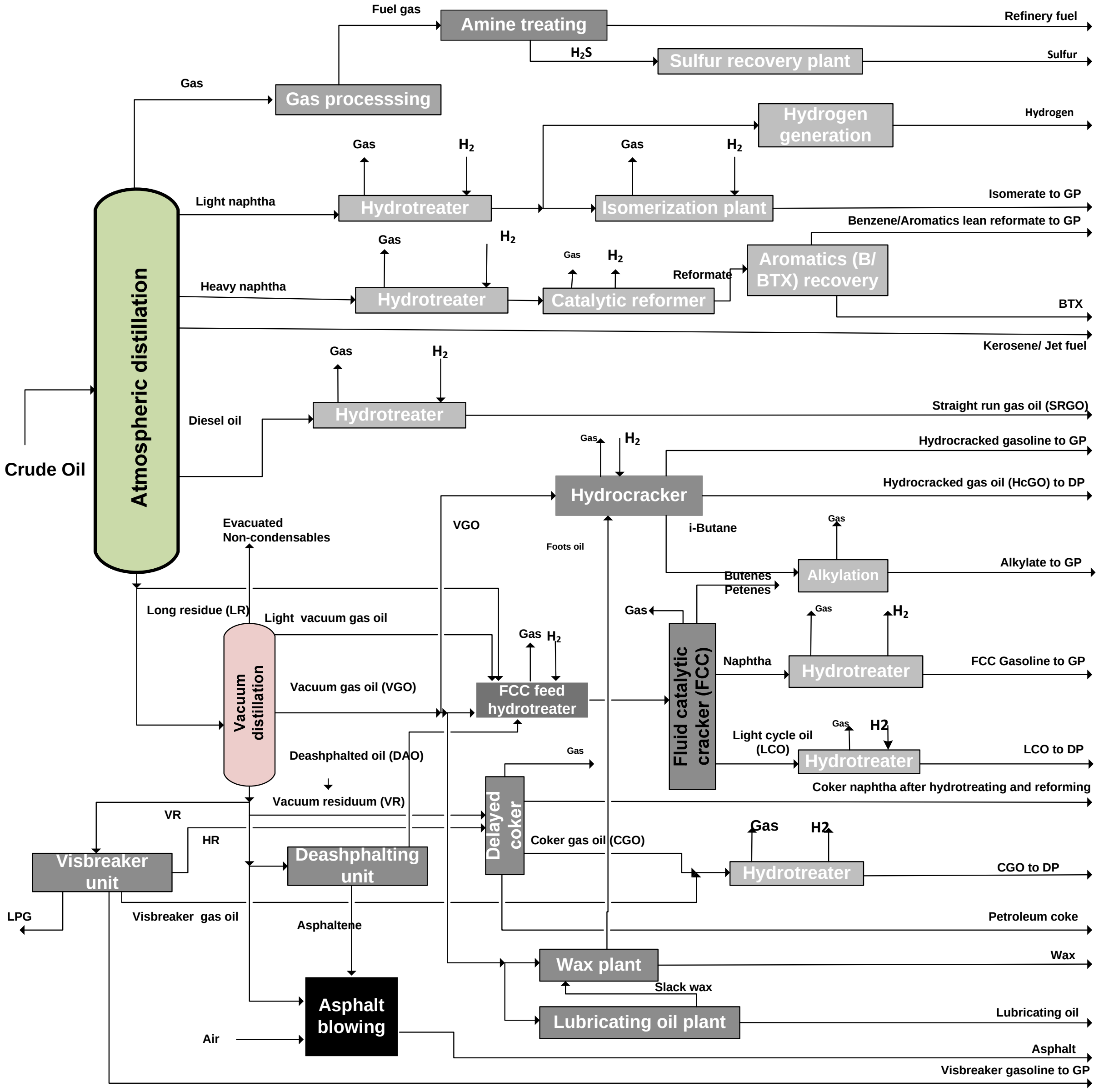


Figure 1.1. Schematic of crude processing in modern refinery (BTX: Benzene, toluene, xylene; LPG: Liquefied petroleum gas; HR: Heavy residue; GP: Gasoline pool; DP: Diesel pool;).

1.2. PRODUCTION OF GAS OIL IN REFINERY

In a modern refinery, several processes produce streams having boiling range similar to gas oil. The gas oil generation in a refinery is presented in Figure 1.2 for better understanding. Straight run gas oil (SRGO) is produced from the crude processing in the atmospheric distillation column (ADC). Light cycle gas oil (LCO) and coker gas oil (CGO), visbreaker gas oil (VbGO) are generated by processing of heavy fraction of crude oil such as vacuum gas oil (VGO), deasphlated oil (DAO), long residue (LR), foots oil, extract streams, etc. in fluid catalytic cracker unit (FCCU), delayed cocker unit (DCU) and visbreaker unit, respectively. FCCU works on the principle of catalytic cracking, whereas, DCU and visbreakers on thermal cracking. Therefore, gas oil streams generated from catalytic and thermal cracking of heavy feed stocks in FCCU, DCU, visbreakers would have significantly different concentration of paraffinic, aromatics and refractive sulfur compounds in comparison to SRGO generated from ADC without any cracking.

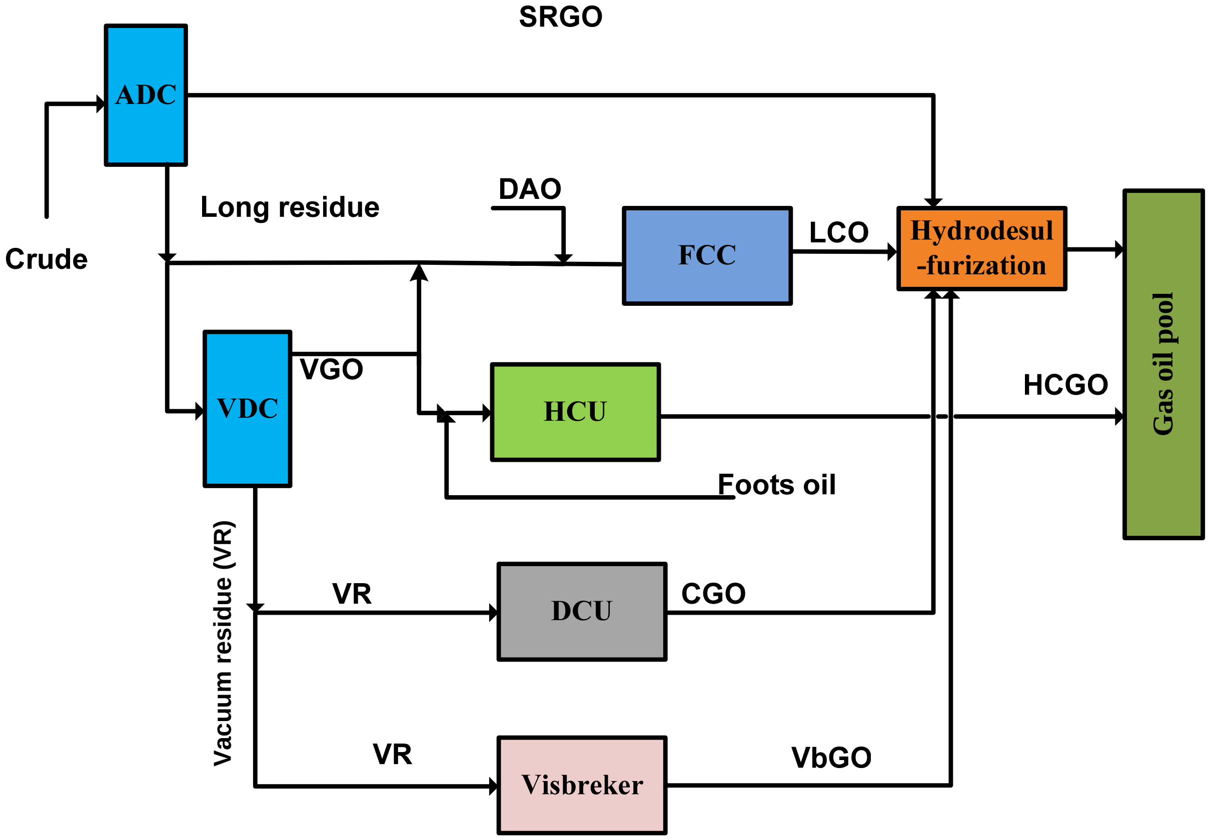


Figure 1.2. Schematic for various gas oil generation in refinery (VDU: Vacuum distillation column).

The gas oil generated from FCCU and DCU will have higher and refractive sulfur content due to properties of their heavy feed stocks. LCO and CGO generated from FCC and DCU has very high concentration of aromatics and polyaromatics (about 80-90%). Cetane number of aromatic compounds is significantly lower whereas the density is significantly higher than the nonaromatic compounds. Thus, higher concentration of aromatics results in very low cetane number and higher density of LCO (Babich and Moulijn, 2002; Sharma et al., 2013). In the refinery, it is a common practice to desulfurize these streams using the HDS. Further, gas oil is also generated from hydrocracker unit by processing of the vacuum gas oil. However, hydrocracker are designed and operated at very sever operating conditions of temperature, pressure and hydrogen to oil ratio. Thereby, hydrocracker gas oil (HcGO) has very low sulfur and high cetane number. This is directly blended in gas oil pool with other hydrotreated gas oil streams.

1.3. DRIVERS FOR DEEP SULFUR AND POLYAROMATICS REMOVAL FROM GAS OIL

1.3.1. Environmental and Health Hazards

Gas oil is composed of paraffins, naphthenes, aromatics, sulfur and nitrogen hydrocarbon compounds. Presence of sulfur (disulfuides, sulphides, thiophenes, benzothiophenes (BT), and dibenzothiophene (DBT) and their alkylated derivatives), diaromatcis (naphthalene and its alkylated derivatives, bi-phenyls, fluorenes), poly aromatics (phenanthrene, anthracene, fluoranthene, pyrene and their alkylated derivatives) and nitrogen (anilines, pyridines, pyrrole, indole, quinoline, carbazole) compounds in gas oil contribute to harmful emissions and are undesirable (EPA, 1999; Chawla, 1997; Ismagilov et al., 2011; Srivastava 2012; Sharma et al., 2013). Sulfur compounds are converted into harmful sulfur oxides (SO_x) and sulfate particulate. Nitrogen compounds are oxidized to nitrogen oxides (NO_x). The quantity of harmful emission of NO_x, SO_x, CO, CO_2, unburnt hydrocarbon (HC) and PM, PAH to environment by the combustion of gas oil in engine strongly depends on the concentration of sulfur and polyaromatics compounds and increases with an increase in gas oil's sulfur content (DECSE Program- Phase I Interim Data Report No. 3, 1999; DECSE Program-final report, 2001; Veinblat et al., 2001; Merkisz and Kozak, 2002; Oh et al., 2003; Phirun et al., 2005; Ristovski et al., 2006; Walsh, 2006). The dissolution of SO_x, particularly SO_3, in water vapor generates H_2SO_4 which results in formation of ultrafine particles in gas oil exhaust which has ability to penetrate into the lungs. It is reported that PM emission from a gas oil engine increases by about 29% with an increase of sulfur content from 3 ppmw to 350 ppmw (DECSE Program- Phase I Interim Data Report No. 3, 1999; DECSE Program-final report, 2001) and decreases by 14% on reducing the sulfur content of fuel from 368 ppmw to 54 ppmw (DACET- final report, 1999). The effect of aromatic content, density, cetane number and distillation temperature corresponding to 90% vaporization of feed (T_{90}) on the exhaust emissions has also been reported in many studies (Ullman et al., 1990; Tsurutani et al., 1995; Paris and Knowles, 1996; Karonis et al., 1998; Matsumura et al., 1999; Uchida and Akasaka, 1999; Kidoguchi et al., 2000; Yanga et al., 2005**)**. A comprehensive impact evaluation of density, cetane number, T_{90} and polyaromatics content of gas oil on the emissions from 19 light-duty vehicles was presented by European programs on emissions, fuels and engine technologies (EPEFE) (Hublin et al., 1996; Vehicle Emissions Reduction, 2014). The generalized outcomes of the study are shown in Table 1.1. It can be seen from the table that improvement in these properties generally reduces the PM and NO_x.

The harmful emissions such as NO_x, SO_x, CO, CO_2, unburnt hydrocarbon (HC) and PM from gas oil exhaust to environment will lead to serious environmental and health concerns such as smog, global warming, acid rain, lung cancer, provocation of respiratory and cardiovascular diseases, aggravation of existing asthma, chronic bronchitis (Koch et al., 1996; Shiraishi et al., 1998; Whitehurst et al., 1998; Stanislaus et al., 2010; Srivastava, 2012; Sharma et al., 2013).

Table 1.1. Impact of fuel composition and properties change on emission of light duty diesel vehicle (Hublin et al., 1996; Vehicle Emissions Reduction, 2014).

Change	Indirect Injection		Direct Injection PM	
	NO_x	PM	NO_x	PM
Increase cetane (50-58)	Very small increase	No effect	Very small increase	Small increase
Decrease density (0.855-0.828)	No effect	Large decrease	Small increase	Large decrease
Decrease T95 (371-326°C)	Very small increase	No effect	Small increase	Small decrease
Decrease polycyclics (9-1%)	Very small decrease	Very Small decrease	Very small decrease	Small decrease

1.3.2. Advancement in Emission Control Device

It is clear from above discussion that harmful emissions can be reduced to much extent by using the low sulfur, high cetane and low polyaromatics gas oil. However, it is vital to note that complete benefits of emission reduction can only be achieved by implementing improved emission control technologies/devices (ECD) which includes diesel oxidation catalyst (DOC), filter for absorption of NO_x and PM, and selective catalyst reduction system.

Oxidation catalyst converts the CO, HC and the soluble organic fraction of the PM present in engine exhaust to CO_2 and H_2O. High sulfur content of fuel also results in formation of high level of hazardous sulfate in the emission due to enhanced oxidation rate of SO_2 by DOCs (DECSE Program-final report, 2001; DECSE Program- Phase I Interim Data Report No. 3, 1999; Corro, 2002). Moreover, sulfur compounds poison the oxidation catalysts of catalytic converters and thus reduce their effectiveness for the oxidation of soluble organic fraction (SOF), CO and HC (EES, 2012; CFT, 2009; AECC, 2000; DECSE, 2001; Koltai et al., 2002). The high level of sulfur in fuel also affects the performance of PM filter and NO_x absorber adversely (Stanislaus et al., 2010). Sulfur affects these emission control devices due to its strong adsorbing tendency on the precious metal catalysts and thereby preventing the adsorption and reaction of hydrocarbons, NO_x, and carbon monoxide (USEPA, 2014). In addition, sulfur compounds also cause corrosion to the parts of internal combustion engines because of the formation of the oxyacids of sulfur from combustion products (Collins et al. 1997). Therefore, automobile manufacturers demand deep removal of sulfur compounds from gas oil to improve the performance of emission control ECD to be used for exhaust after-treatment to reduce overall emissions from vehicles.

1.3.3. Environmental Legislation on Diesel Fuel Specification

Environmental regulations have been implemented across the globe to limit the sulfur and aromatic content of gas oil with the aim of improving the air quality by reducing the direct harmful emission and overall hazardous emission by facilitating the implementation of advance emission control devices (EES, 2012; CFT, 2009). Detailed specification of gas oil implemented in major countries such as USA, European Union, China, Republic of Korea, Austraila, Sweden, etc. has been reported in various studies (Stanislaus et al., 2010; Sharma et al., 2013).

The strictest specifications for clean gas oil has been proposed by worldwide fuel character (WWFC) and are given in Table 1.2 (Courty and Gruson, 2001; Sharma et al., 2013). WWFC has proposed increased cetane index, significant reduced level of PAHs, and lower T_{95} distillate temperature in addition to ultra low sulfur level specifications of gas oil (Worldwide fuel charter, 2006; Sharma et al., 2013).

Evolution of gas oil fuel quality in India started in 1995 with cetane number (CN) of 45 and sulfur content (SC) of 1 wt.%. These specifications were revised in 1996 (SC=0.5% : Delhi + selected cities), 1998 (SC =0.25% : Delhi), 2000 (CN=48; SC=0.25%: Nationwide), 2001 (SC= 0.05%: Delhi + selected cities), 2005 (SC=350 ppmw: selected 2010 (SC=350 ppmw) and in 2010 (SC=50 ppmw; selected areas) (DS, 2015). The adoption of regulations for fuels and vehicle emissions in India is based on European standards. Table 1.3 shows the diesel specifications as per various bharat-stage (BS) norms in India (BSN, 2015).

Therefore, reduction in sulfur content of fuel to meet the specification imposed by environmental regulations can trim down the harmful emissions by reducing emission of sulfur dioxide (SO_2) and sulfate PM due to improved fuel properties, by enhancing the performance of emission control devices and by facilitating the implementation of new advanced emission control technologies such as PM filters, NO_x absorbers, etc.

Table 1.2. Worldwide fuel charter (WWFC) diesel fuel specifications (Worldwide fuel charter, 2006).

Property	Category 1	Category 2	Category 3	Category 4
Density (g/cm^3)	0.860	0.850	0.840	0.840
Sulfur (ppmw)	2000	300	50	10
Cetane index	45	48	50	52
Cetane number	48	51	53	55
Aromatics (wt.%)	-	25	20	15
PAH (wt.%)	-	5	3	2
T_{90} (max.°C)	-	340	320	320
T_{95} (max.°C)	370	355	340	340

Table 1.3. Diesel specification in India.

Characteristic	BSII	BSIII	BSIV
Density @15^{0}C (kg/m$^{3)}$	820-800	820-845	820-845
Sulfur content (mg/kg max.)	500	350	50
Cetane number (min.)	48	51	51
Cetane index	46	46	46
Polycyclic aromatic hydrocarbon	-	11	11
Distillation			
Min. Reco. @ 350°C	85	-	-
Min. Reco. @ 370°C	95	-	-
Max temp. for 95vol.% Recovery (°C)	-	360	360

1.4. DESULFURIZATION PROCESS

Currently, refining industry is facing serious challenges of meeting the increasing demand of clean gas oil. This challenge shall become more serious in future due to necessity of processing the heavy sour crudes due to their increased availability. Researchers and technologist are putting serious efforts for exploring desulfurization processes which can produce ultra lower sulfur diesel in a cost effective and environment friendly way.

1.4.1. Hydrodesulfurization (HDS)

Presently, hydrotreating process is most widely used process to produce the clean transportation fuels in the refinery. The success of hydrdesulfurization (HDS) is attributed to its industrial proveness and in place already huge infrastructure and facilities for advance research for its continuous improvement to build grass-roots units with minimum failure risk (Ismagilov et al., 2011). HDS is usually carried-out over supported catalysts containing sulfides of Co-Mo or Ni-Mo or combination thereof on alumina in the temperature and hydrogen partial pressure ranges of 320–400°C and 20–60 bars, respectively (Gates and Topsoe, 1997; Lecrenay et al., 1997; Song, 2003; Ismagilov et al., 2011). Various studies have reported that relative reactivity of different sulfur compounds such as thiophene (TH), benzothiophene (BT), dibenzothiophene (DBT), 4-methy dibenzothiophene (4-MDBT), 4,6-dimethyldibenzothiophene (4,6-DMDBT), 2,3,6-trimethy dibenzothiophene (2,3,6-TMDBT) is significantly different (Nag et al., 1979; Kabe et al., 1993; Houalla et al., 1980; Andari et al., 1996; Knudsen et al., 1999; Shafi et al., 2000). Robinson and Dolbear (2006) reported that rate of HDS is strong function of molecular structure of sulfur compound. The relative rates of various sulfur compounds have been tabulated in Table 1.4 (Robinson and Dolbear, 2006).

It can be seen that HDS reactivity for sulfur compounds followed the order: TH > BT > DBT > 4-MDBT > 4,6-DMDBT > 2,3,6-TMDBT. It is clear that alkyl substituted dibenzothiophes and debenzonapthiophene are highly refractive sulfur compounds for desulfurization. The biggest challenge in the production ultra low sulfur gas oil is the removal of the least reactive sterically hindered alkyl DBTs along with various poisons such as aromatics, particularly polyaromatics and nitrogen compounds in gas oil and H_2S content in circulating hydrogen which affects their activity adversely under deep desulfurization conditions.

Various researchers have investigated the influence of aromatic compounds on deep desulfurization of gas oil. It has been reported that the adverse effect of polyaromatics on desulfurization for 4,6-DMDBT is more pronounced than that for DBT (Koltai et al., 2002; Chen et al., 2005 ; Egorova and Prins, 2004; Song et al., 2006). Extent of inhibition depends on the size of aromatic molecule which affects its adsorption coefficients on hydrogenation site on the catalyst (adsorption constant for 3-ring phenanthrene molecule is about six times higher than the 2-ring naphthalene molecule) and thus competes with sulfur (Ismagilov et al., 2011). Presence of nitrogen compounds in gas oil also negatively impacts the HDS reactions due to strong adsorption tendency and neutralization of acidic site of active catalytic sites (Zeuthen et al., 2001; Koltai et al., 2002; Ismagilov et al., 2011). The partial pressure of H_2S in the reaction system also influences the desulfurization and sensitivities of NiMo and CoMo catalysts to H_2S poisoning (Kabe et al., 2001).

Table 1.4. Relative rate of hydrodesulfurization of different sulfur compounds (Robinson and Dolbear, 2006).

Sulfur compound	Relative HDS rate	Remark
Thiophene	100	Easy
Benzothiophene	50	Easy
Dibenzothiophene	30	Difficult
4-Methy dibenzothiophene	5	More difficult
4,6-Dimethyldibenzothiophene	1	Most difficult
2,3,6-Trimethy dibenzothiophene	1	Most difficult

The quality of the gas oil is measured in term of concentration of different type of sulfur, aromatics and nitrogen compounds having different reactivity and boiling range. Origin of the crude and process from which gas oil is generated governs the sulfur, aromatic nitrogen level and combustion properties of gas oil. Boiling range of gas oil also affects the concentration of these compounds in gas oil. Thus, quality of gas oil plays a major role in its deep desulfurization to ultra low level. Detail of feed quality affect on desulfurization performance has been discussed in a review paper published by Stanislaus et al. (2010).

1.4.1.1. Revamping of existing hydrotreaters for deep sulfur removal

Various studies suggest that revamp and modification of existing hydrotreaters which were designed and installed in the refineries to meet the sulfur specification in the range of 350 -500 ppmw is possible to meet the sulfur specification in the range of 10-15 ppmw. The following possible operational solutions are suggested for improvement in sulfur removal in an existing gas oil hydrotreater (Palmer and Torrisi, 2003; Sayles et al., 2004; Ismagilov et al., 2011):

- Managing feed quality (by reducing the end boiling point; using easier feed having lower concentration of refractive sulfur, polyaromatics and nitrogen compounds)
- Replacing the existing catalyst by high activity catalyst
- Increase in operation severity (increased start of run temperature, increase in hydrogen pressure, higher hydrogen to oil ratio, lower weight hour space velocity)
- Increase in catalyst amount (by use of additional reactor, dense loading, etc.)
- Increasing purity of recycled and make up hydrogen (by removing the C1-C4 hydrocarbons, H_2S and NH_3 from recycled gas)
- Improving the feed distributor in the reactor feed for improved liquid-solid contact

It may be mentioned that selection of appropriate option or combination of options to achieve the sulfur target level in a cost effective way will depend on refinery configuration, existing hydrotreaters design parameters, hydrogen availability, etc. Revamp study for improving the existing hydrotreaters to produce the gas oil of less than 15 ppmw sulfur reveals the needs of substantial retrofitting in term of installation of additional reactor to increase the catalyst volume, reengineering of reactor internals configuration for improved liquid-solid contacting, purchase and storage of more reactive catalyst, installation of new equipments or revamp of existing equipments such as H_2 makeup compressor due to significant increase in hydrogen consumption, installation of pressure swing adsorption for increasing the purity of hydrogen, recycle gas compressor due to increased recycle gas flow and pressure drop, strippers and separation vessels due to hydraulic issues, and the amine treating unit for deep H_2S removal and handling the increased amount of recycle gas. Moreover, application of extremely sever operating conditions (high temperature and pressure) deep removal of sulfur and aromatic compounds leads to huge consumptions of operating utility such as steam, cooling water, electricity, etc. and thus will increase the green house gases (GHG) emissions to environment noticeably. Application of very reactive catalyst and sever operating conditions results in significant aromatic saturation which leads to significantly increased H_2 consumption. This may result in either installation of new grass root hydrogen plant or revamp of existing H_2 plant for capacity enhancement. It can be inferred from the above discussion that revamp of existing hydrotreating facilities need large number of modification and considerable amount of capital (Palmer and Torrisi, 2003; Ismagilov et al., 2011; Sharma et al., 2013). Overall, deep sulfur removal from gas oil using the HDS is quite a costly option and there is urgent need to investigate the alternative cost effective and environment friendly methods of desulfurization by the researchers.

1.4.2. Non-hydrodesulfurization Processes

Various researchers are working in the area of development of non-HDS methods which include oxidative desulfurizataion (ODS) (Yazu et al., 2004; Zhao et al., 2007; Al-Shahrani et al., 2007; Castillo et al., 2009; Arellano et al., 2014; Arellano et al., 2015), selective adsorptive desulfurization (ADS) (Takahashi et al., 2002; McKinley and Angelici, 2003; Hernandez-Maldonado and Yang, 2003; Hussain and Tatarchuk, 2013; Xiao et al., 2015), biodesulfurization (BDS) (Guchhait et al., 2005: Agarwal and Sharma, 2010; Bhatia and Sharma, 2010), and solvent extraction desulfurization (SEDS) (Bösmann et al., 2001; Gaile et al., 2010a; Rodríguez-Cabo et al., 2013) that have the potential to be used either as stand alone or as complementary method with HDS for cost effective production of ultra clean gas oil. These processes have been briefly discussed in the subsequent sections along with their major benefits and limitations.

1.4.2.1. Oxidative desulfurization (ODS)

ODS is a one of the promising processes for deep reduction of sulfur at significantly lower temperature and pressure conditions (Ali et al., 2006). ODS involves oxidation of sulfur compounds to sulfoxides and sulfones for changing their polarity, freezing point, and boiling point to facilitate easier separation of sulfur compounds using separation methods like solvent extraction (Otsuki et al., 2000; Hassan et al., 2013; Maity et al., 2014), adsorption (Etemadi and Yen, 2007), distillation (Dolbear and Skov, 2000) and precipitation from the organic phase. Various oxidants such as hydrogen peroxide (Collins et al., 1997; Yazu et al., 2001; Hulea et al., 2001; Palomeque et al., 2002; Anisimov et al., 2003; Shiraishi et al., 2004; Chica et al., 2006; Zhu et al., 2006; Zhao et al., 2009; Jose et al., 2011; Gonzalez et al., 2012; Maity et al., 2014) or organic tertiary butyl hydroperoxides (*t*-BuOOH (Wang et al., 2003; Ishihara et al., 2005; Chica et al., 2006; Al-shahrani et al., 2007a,b; Prasad et al, 2008; Arellano et al., 2014; Arellano et al., 2015) and peracids (Gore, 2000; Gore et al., 2003), ozone, nitrogen oxides, oxygen, nitric acid (Ford et al., 1967; Rang et al., 2006) and sulfuric acid (Sharipov et al., 1991; Levy et al., 2003) have been used to carry out the ODS in the presence of homogeneous (acetic, formic, and other acids) (Sharipov et al., 1991; Trakarnpruk et al., 2009; Qiu et al., 2009; Dehkordi et al., 2009; Gonzalez et al.,2012) or heterogeneous (oxides of V, W, Mo, Mn, Co, Fe supported on Al_2O_3, SiO_2, TiO_2, sulfated ZrO_2; titanium silicate, sulfur doped activated carbon) (Otsuki et al., 2000; Gore et al., 2003; Wang et al., 2003; Chica et al., 2006; Ali et al., 2006; Ito et al., 2006; Prasad et al., 2008; Lu et al., 2008; Cansigno et al., 2012; Sengupta et al., 2012; Maity et al., 2012; Seredych et al., 2013; Saha and Sengupta, 2015) catalysts without or with ultrasound external energy (Bhasarkar et al., 2013, 2015a). It is vital to note that an extensive research work has been conducted on ODS over the years and even pilot and small commercial plants had been demonstrated. Still there is long way to arrive at for its large scale commercialization in the refinery. Some of the associated challenges with ODS include reaction selectivity, safety, equipments cost and separation cost. Most of the catalytic systems and oxidants reported are toxic and expensive. The use of homogenous catalyst which shows high activity and selectivity poses difficulty in their recovery for reuse. The quantitative chemical consumption of conventional oxidants such as hydrogen peroxide (H_2O_2), tertiary butyl hydrogen peroxide (TBHP), etc. is much higher than the H_2 due to drastic difference in their molecular weight and leads to its feasible application for low sulfur fuel (less than 500 ppmw) only. There is also requirement of new facility to be installed for generation of oxidant source in the refinery. Air oxidation with heterogeneous catalyst based ODS seems practical to overcome the problem of oxidant handling, but selectivity and effectiveness of air based oxidation is not proven. Thus, development of a ODS process which works on mild oxidation reaction conditions, with heterogeneous catalyst at high selectively for oxidizing the sulfur compounds with inexpensive oxidant such as air can address the ODS issues for its implementation in the industry.

1.4.2.2. Adsorptive desulfurization (ADS)

During the adsorptive desulfurization of gas oil, sulfur compounds from other hydrocarbons are separated by their preferred adsorption on the adsorptive material such as molecular sieves, zeolites, aluminosilicates, coal, activated carbon (AC) and its modifications, alumina, zinc oxide, TiO_2-CeO_2, silver-titania –alumina, metal–organic frameworks (MOF), etc. (Lee et al., 2002; Larrubia et al., 2002; Hernandez and Yang, 2004; Sano et al., 2005; Tang et al., 2008; Shalaby et al., 2009; Achmann et al., 2010; Nair and Tatarchuk, 2011; Seredych et al., 2012; Hussain and Tatarchuk, 2012; Hussain et al., 2012; Xiao et al., 2012, 2013; Arcibar-Orozcoet et al., 2013; Yu et al., 2013; Wu et al., 2014; Hussain and Tatarchuk, 2014). Low temperature operation of ADS for removing the refractive sulfur compounds is one of its major advantages over HDS. However, there is a need to address various challenges associated with ADS prior to commercialization stage. These challenges include development of adsorbents with high adsorption capacity and high selectively for aromatic sulfur compounds over the other aromatic compounds present in gas oil, removing difficulties associated with regeneration of effective adsorbents using either solvent washing or calcinations (Hernandez and Yang, 2004). In the former method, removal of sulfur compounds and other hydrocarbon from organic solvent is quite difficult, capital and energy intensive. In the calcination method, sulfur and aromatic compounds are burned which leads to loss of valuable materials and also loss of adsorbent surface area due to sintering. Removal of high sulfur saturates the adsorption bed very fast. This will require large and multiple adsorbent beds to minimize the number of turnovers and would leads to piles of spent adsorbents. Thus, ADS application may be practically feasible only for low sulfur fuel as polishing with very selective and easily regeneratable adsorbent.

1.4.2.3. Biodesulfurization (BDS)

BDS involves either bio-transformation of sulfur compounds like DBT or its consumption as energy source by bacterial and microbial species such as *Arthrobacter, Brevibacterium, Pseudomonas, Gordona, and Rhodococcus spp* (Kirimura et al., 2001; Li et al., 2005; Hou et al., 2005; Guchhait et al., 2005b; Gunam et al., 2006; Guobin et al., 2006; Yu et al., 2006; Li et al., 2007; Caro et al., 2007; Mohebali et al., 2007; Chen et al., 2008a, 2008b; Alves et al., 2008; Madeira et al., 2008). Several authors reported the BDS of liquid fuels for studying the various aspects involved such a performance of bacterial and microbial species for desulfurization, designing and mathematical modelling of biodesulfurizer including trickle bed and kinetics, and integration of biorefining with petroleum refineries, etc. (Pacheco, 1999; Guchhait et al., 2005a; Mukhopadhyaya et al., 2005; Chowdhury and Duttagupta, 2005; Bhatia and Sharma, 2006; Mukhopadhyaya et al., 2007; Bhatia and Sharma, 2012; Bhasarkar et al., 2015b). Major benefits of BDS are its ability to remove sulfur compounds with substantially less GHG emission, with lower capital and operating costs. However, BDS has many limitations that prevent it from being implemented at commercial scale. The major issues needed to be addressed in BDS are slow metabolism of sulfur compounds in comparison to other desulfurization methods, need of large amount of biomass (typically 2.5 g biomass per g of sulfur) and requirement to keep alive a biological systems to function under variable input conditions of pH, temperature and dissolved oxygen concentration found in refineries, and difficulties associated with separation of the cells from oil. Moreover, cost of biocatalyst and its mass production with high desulfurization activity, efficient reactor design and complication involved in oil-water mixture separation are some of the other issues to be resolved for BDS commercialization (Monticello, 2000; Guobin et al., 2006).

1.4.2.4. Solvent extractive desulfurization (SEDS)

SEDS is based on the principle of difference in the solubility of sulfur and other hydrocarbon compounds in a solvent. Solvent extraction process involves removal of impurities via scrubbing the hydrocarbon stream with solvent and recovery of solvent from solvent and hydrocarbon rich phases for its reuse. Application of solvent extraction for dearomatization and aromatic production is well established on the commercial and industrial scale due to its specific characteristics of low pressure and temperature operation, easy regeneration of solvent for reuse and does not involve any reaction, catalysts and oxidizing regent (Sharma et al., 2013). However, application of solvent extraction for desulfurization on industrial scale in not well established, but many researchers are working in this area (Petkov et al., 2004; Huang et al., 2004; Gaile et al., 2006; Toteva et al., 2007; Gaile, 2008; El-Aty et al., 2009; Hassan et al., 2009; Gaile et al., 2010a,b; Ke-dra-Krolik et al., 2011; Chen et al., 2012; Wilfred et al. 2012) Dharaskar et al., 2014; Chen et al., 2014; Kianpour et. al., 2014; Shao et. al. 2014; Kumar et al., 2015). Solvent extraction seems to be one of the best choices for removing refractive sulfur compounds or oxidised sulfur compounds along with poly-aromatics, and heterocyclic nitrogen compounds from gas oil (Ismagilov et al., 2011; Kumar et al., 2014). Detailed literature review of SEDS process for gas oil is given in Chapter 2.

1.5. CURRENT RESEARCH GAP

An exhaustive literature review presented in Chapter 2 reveals that though various studies have been reported on SEDS still there are various aspects which have not been addressed in previous studies for its implementation in the refinery. The major gaps which need to be investigated are listed in subsequent sub sections.

1.5.1. Computational Studies

- Studies include only TH, BT and DBT sulfur compound for solvents screening for desulfurization. Studies do not include the *alkylated derivatives* of BT and DBT which are more difficult to remove in HDS than BT and DBT.
- Ionic liquid solvents only have been evaluated for desulfurization. No study compares the overall effectiveness of both ILs and well established organic solvent for desulfurization.
- Studies consider only capacity, selectivity and performance index estimated at infinite dilution as performance indicator for solvent ranking for desulfurization. No study considers the effect of complexity of solvent recovery section (governed by boiling point of solvent) which affects the extraction process capital and operating cost, significantly, for solvent performance evaluation.

1.5.2. Experimental Studies

- Most of the studies are on straight run gas oil (SRGO) desulfurization except few which are on hydrotreated SRGO and VGO.
- Studies used degree of sulfur removal (D_{sr}) without or with yield of desulfurized gas oil as their main objective. There is no study in literature which put emphasis on reverse effect of capacity and selectivity of solvents to evaluate the effectiveness of solvent for sulfur removal from gas oil.
- There is no comprehensive study which reports the effect of solvent nature, solvent to feed ratio, extraction temperature and water concentration in main solvent on degree of sulfur removal and yield of desulfurizatized gas oil.
- Although usage of water as an anti-solvent in the aromatic removal process is well established, its usage in sulfur removal extraction process is reported in very few studies only.
- Experimental extractive desulfurization studies reported in literature were carried out either in batch single stage or continuous with discrete multistage to study the degree of sulfur removal and yield of extracted gas oil. The packed bed extractor application is well established in commercial extraction process in industries. However, no desulfurization study has been carried out in continuous counter current packed bed column so as to understand the effect and optimization of operating parameters on the sulfur removal and yield of extracted SRGO (ESRGO).
- The optimization of operating conditions for extractive desulfurization of SRGO to maximize the removal of sulfur with maximum yield had not been explored.
- In refinery, various gas oil streams (SRGO, LCO, CGO) having much different composition are generated. There is no study reported that demonstrates the effect of gas oil composition on solvent extractive desulfurization process performance parameters.
- There is hardly any study in the literature which addresses issues related to minimize the loss of hydrocarbons with extract and value addition to extract hydrocarbon for its effective utilization as product.

1.6 OBJECTIVES

In view of identified research gaps based on exhaustive literature review, following objectives were set for the present study.

- To establish a practical and realistic strategy (using computational approach) for solvent evaluation with respect to desulfurization and denitrification of gas oil based on industrial usability and process complexity of recovery solvent section.
- To carry out experimental evaluation of industrially proven and viable organic solvents for removal of sulfur and aromatic compounds from SRGO in single stage-mixture settler and continuous packed bed column solvent extraction systems.
    - To optimize the operating variables for desulfurization of SRGO in a packed bed extractor using parametric study and multiple response optimizations with desirability function approach to maximize sulfur removal and yield of extracted straight run gas oil (ESRGO).
- To evaluate the quantitative effect of molecular structure of sulfur compounds and carrier phase composition in a synthetic gas oil on SEDS performance parameters
- To evaluate the effect of composition of different actual gas oil streams (SRGO, LCO, CGO and their mixture termed as mixed gas oil (MGO) on solvent extraction process using N-methyl-2-pyrrolidone (NMP) as solvent and water as anti-solvent in batch and packed bed extractor.
- To explore the possible methods for minimizing the loss of valuable hydrocarbons with extract, quality improvement of extract hydrocarbon for its utilization as carbon black feed stock (CBFS) and for extract utilization in other secondary conversion processes.

1.7. THESIS ORGANIZATION

The thesis contains 6 chapters. Chapter 2 presents a brief literature review on computational and experimental studies carried out in batch single stage and multi discrete stage continuous extractor for desulfurization of gas oil using organic solvents, co-solvents, anti-solvents and ionic liquid solvents. Work done in the present study based on the objectives given in section 1.6 is presented in chapters 3-5. A new strategy (using computational approach) for solvent evaluation with respect to desulfurization and denitrification of gas oil based on industrial usability and process complexity of recovery solvent section is reported in Chapter 3. Work done on extraction of SRGO in batch single and multi stages as well as continuous packed bed extractor using well established organic solvents is presented in chapter 4. Effects of operating conditions such as solvent to feed ratio, extraction temperature, water (anti-solvent) content in main solvent on degree of sulfur removal and yield of desulfurized gas oil are reported in chapter 4. The optimization of these operating conditions for maximizing the degree of sulfur removal and raffinate yield in packed bed extractor is also presented in chapter 4. Chapter 5 presents studies on extraction of synthetic gas oils and real gas oils (SRGO, LCO, CGO and their mixture) in a batch single stage and continuous packed bed column under various operating conditions. The method to minimize the loss of desired material with extract and to improve the quality of extract is also reported in this chapter. Conclusions of overall present study and recommendations for future work are given in chapter 6.

Chapter – 2

LITERATURE REVIEW

2.1. GENERAL

Extractive desulfurization is one of the areas in which several researchers are working to evolve a cost effective and environmentally benign desulfurization process. Several studies have been reported on the application of solvent extraction process for removal of sulfur or oxidized sulfur compounds, nitrogen and aromatic compounds from the hydrocarbon streams having boiling range similar to gas oil using organic and ionic liquid solvents (ILs). This chapter presents a literature review of the recent research work carried out in this area. Research gaps identified based on this literature review are given in chapter 1 as section 1.6.

2.2. SOLVENT EXTRACTIVE DESULFURIZATION (SEDS)

2.2.1. Principle of the Process

Solvent extraction is based on the principle of difference in the solubility of solute compounds in a solvent which depends upon their chemical structure. In solvent extraction, scrubbing of hydrocarbon stream with solvent for removal of impurities generates the hydrocarbon rich phase with reduced level of impurity (raffinate phase) and solvent rich phase (extract phase). The solvent from raffinate and extract phase is recovered for its reuse and to make raffinate and extract hydrocarbon solvent free. Solvent not only control the quality of raffinate and extract but also economics of the process. Thereby, selection of suitable solvent is a key for success of extraction processes.

2.2.2. Performance Indicators Used in Solvent Extraction Studies

The capacity (C_i), selectivity(S_{ij}) and performance (capacity × selectivity) indeces at infinite dilution have been widely used for screening and evaluation of the solvents using the computational approach (Kumar and Banerjee, 2009; Anantharaj and Banerjee, 2011a, 2011b). In the experimental studies, many investigations have also used either one or multiple indicators such as extraction factor (ε_S), distribution coefficient (K_S), degree of sulfur removal (D_{sr}), yield (Y) of desulfurized gas oil, capacity C_i and S_{ij} for evaluation of the performance of solvents for desulfurization, dearomatization and denitrification of gas oil (Lo et al., 1983; Petkov et al., 2004; Gaile et al., 2006; Toteva et al., 2007; Gaile, 2008; Gaile et al., 2010a,b; El-Aty et al., 2009; Hassan et al. 2009). The definition and expression of these indicators are given in chapter 4.

2.2.3. Extraction Apparatus Configurations

Generally, single stage and multistage counter current continuous solvent extraction processes are used for desulfurization and dearomatization of liquid fuels**.** Jacketed mixer-settler, glass reactor equipped with stirrer and separating funnels were generally used in laboratory for evaluation of solvent performance in single stage (Treybal, 1951; Lo et al., 1983; Gail et al., 2006; Gaile et al., 2010a). Hydrocarbon and solvent are mixed in the extractor for extraction to occur, and hydrocarbon and solvent rich phases are settled for their removal. At the best, the insoluble phases may be in equilibrium and performance can be represented as one single theoretical stage. Multistage counter current continuous processes are carried out either with discrete stage type contacting using a series of mixture-settler or separating funnels and with continuous contacting using packed column. However, in the industry continuous counter current extraction is mostly carried out using the vertical column with or without internal devices (packing/trays) which influence the flow pattern of solvent and hydrocarbon phases (Treybal, 1951; Lo et al., 1983). Based on the internal design, these columns are known as spray, packed, sieve tray and rotating disk extractors. Among these extractors, application of packed column is well established for aromatic production in the industry using solvent extraction process.

2.3. SOLVENT EXTRACTIVE DESULFURIZATION OF GAS OIL

Conventional hydrodesulfurization (HDS) process of gas oil is not capable of removing sulfur from alkyl DBT compounds because of the steric hindrance from the alkyl group attachment. A numbers of solutions for improving the performance of hydrotreaters for reducing the gas oil sulfur content upto ultra low level have been suggested. These solutions include higher temperature and pressure of the reactor, more active catalyst, longer residence time, large volume of catalyst or addition reactor, higher H_2 partial pressure, H_2S free hydrogen application and cleaner feed, etc. However, these changes would require huge additional investments and would also lead to significantly increased CO_2 emissions to atmosphere. Selective solvent extractive desulfurization (SEDS) is capable of removing the refractive sulfur, aromatics particularly, polyaromatics and nitrogen compounds to a great extent. It operates at low temperature and pressure, requires low energy consumption, no need of expensive H_2, and no need of special equipments such as high pressure reactor and compressor, etc. Therefore, SEDS seems to be an attractive complementary process to hydrotreaters to produce ultra low sulfur gas oil at low operating and capital cost.

2.3.1. Computational Studies

Experimental evaluation of solvents performance using their capacity and selectivity involves number of steps such as generation of liquid-liquid equilibrium data, removal of solvent from raffinate and extract phase compositional analysis of raffinate and extract phase, etc. Chemicals used in the experimental analysis are also very expensive and their disposal to environment is hazardous. Experimental evaluation also needs complicated equipments. Therefore, it is apparent that evaluation of solvents for removal of sulfur and aromatic compounds from gas oil using the experimental approach would be extensively time and resource consuming in comparison to the computation methods. Therefore, molecular simulation based computation approach has been becoming increasingly important in the scientific research and gaining wide spread application in screening and evaluation of various solvent for separation of specific impurity. This approach popularity has been driven by the advancement in the design of computational hardware and simulation algorithms.

Various researchers have reported studies on solvent extraction of sulfur, nitrogen, aromatics compounds from aliphatic hydrocarbon compounds with ILs using the computational tools (Kumar and Banerjee, 2009; Verma et al., 2011; Anantharaj and Banerjee, 2011a,b). The predictive analysis of capacity and selectivity at infinite dilution, performance factor as well vapor and liquid–liquid equilibria data of various ILs have been reported using conductor like screening model along with its extension to real solvents (COSMO-RS) model (Klamt, 2005; Banerjee et al., 2006; Banerjee and Khanna, 2006; Banerjee et al., 2007; Kumar and Banerjee, 2009; Verma et al., 2011). In one study, Kumar and Banerjee (2009) investigated 264 ILs generated from the possible combination of 24 anions and 11 cations for thiophenic sulfur removal from synthetic diesel. Solvents were evaluated using their capacity (C_i) and selectivity (S_{ij}) at infinite dilution and performance index (P_I) indicators which were estimated using infinite dilution activity coefficient predicted with the help of COSMO-RS. It was found that smaller size of cation irrespective of the type shows higher selectivity and lower capacity for the removal of thiophene. There is general trend of increasing selectivities for imidazolium based cations (5.3 to 75.3) in comparison to pyridinium based cations (5.01 to 35.1). For different fluorinated anions, thiophene extraction followed the order: [BF_4] > [PF_6] > [CF_3SO_3] > [BTA] which is similar to increase in their van der Waals volume.

Verma et al. (2011) analyzed the performance of three ionic liquids (1-ethyl-3-methylimidazolium ethyl sulphate ([EMIM][$EtSO_4$]) and 1-ethyl-3-imidazolium acetate

([EMIM][CH_3COO]) for extractive desulfurization of benzothiophene from n-hexane. They estimated the non-random two-liquid (NRTL) and UNIversal QUAsiChemical (UNIQUAC) interaction parameters for each IL using the experimental equilibrium data. Performance of individual and mixed ILs was further analyzed using COSMO-RS model for desulfurization. In another study, performance of 168 ILs resulted from combination of 6 cations and 28 anions for removal of aromatic sulfur compounds such as thiophene (TH), benzothiophene (BT) and dibenzothiophene (DBT) from synthetic diesel prepared by mixing the various paraffinic and aromatics compounds was evaluated using the predicted values of their C_i and S_{ij} at infinite dilution (Anantharaj and Banerjee, 2011a). It was found that selectivity of ILs for sulfur compounds decreases in order: TH (4-24) > BT (2-12) > DBT (1-7). It was also observed that S_{ij} and C_i of ILs at infinite diluation strongly depends on the type of hetero atom (N, S, O) and its location in the cation structure. The cation without the aromatic ring combined with anions having the sterical shielding effect such as [SCN], [CH_3SO_3], [CH_3COO], [Cl], [Br] were found to be the most suitable ILs for desulfurization.

Simultaneous removal of sulfur and nitrogen compounds from the synthetic diesel was investigated by Anantharaj and Banerjee (2011b). For selecting the promising ILs, a computational screening of various ILs was carried out. Study involved a range of ILs prepared by combination of 6 commonly studied cations (1-ethyl-3-methylimidazolium [EMIM], 1-ethyl-1-methylprrolidium [EPY], 1-ethyl-1-methylpyrrolidinium [EPYRO], 4-ethyl-4-methylmorpholium [EMMOR], 1-ethyl-1-methylpiperidium [EMPIP] and 1,2,4-trumethylpyrazolium [TMPYZO]) and 25 anions. For screening the solvent, S_{ij} and C_i at infinite dilution parameters of ILs were estimated from the predicted value of activity coefficient at infinite dilution of sulfur (thiophene, benzothiophene and dibenzothiophene) and nitrogen (pyrrole, indole and indoline, carbazole, benzocarbazole, pyridine, quinoline and benzoquinoline) compounds in ILs using COSMO-RS model. It was observed that presence of electronegative atom in anion increases the IL selectivity. [EPYRO], [EMPIP] and [EMMOR] cations in combination with [Br], [NT], [TfO], [MSACN], [BMA], [BTA],[Me-Et-EtSu], [Dec] and [OcSu] anions were reported as potential ILs for simultaneous sulfur and nitrogen compounds removal from synthetic diesel.

2.3.2. Experimental Studies

2.3.1.1. Organic solvents

The application of organic solvent in aromatic and lube oil production is well established in industry. This leads to their production at large scale and their easy availability in open market. Many investigators have reported removal of sulfur, aromatics and nitrogen compounds from hydrocarbon stream having boiling range equivalent to gas oil using solvent extraction with various organic solvents. The work based on gas oil desulfurization has been summarized and discussed below.

The first commercial extraction set up was installed in United States in 2001 for removal of sulfur and aromatic compounds from diesel fraction (Gaile, 2008). The extractability of model sulfur compounds such as 2-methylthiophene (2-MT), 2,5-dimethylthiophene (2,5-DMT), BT, DBT, 4-dimethyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) dissolved in hexadecane with acetonitrile (ACN) solvent was studied by Cedeño-Caero et al. (2005) in a glass reactor at S/F of 1.0 and extraction temperature (T_E) of 60°C. A magnetic stirrer was used for mixing the solvent and hydrocarbon mixture. It was observed that mixing time of 5 min is enough to reach the equilibrium between extract and raffinate phases. Percent sulfur removal varied in the range of 20% (4,6-DMDBT) to 50% (2-MT). The extractability of sulfur compounds followed the order: 2-MT > BT > 2,5-DMT > DBT > 4-MDBT > 4,6-DMDBT. A batch single stage solvent extraction of synthetic diesel (SC=600 ppmw) prepared by dissolving thee equal weight of thiophene, DBT and 4,6-DMDBT in n-octane was also reported in another study (Bakara, 2012). Extraction was carried out using the organic solvents such as ACN, N, N-diemthylformamide (DMF) and 1-methy-2pyrolidone (NMP) at T_E of 29°C and S/F ratio of 0.2. The ranking of solvents with respect to percent removal of all sulfur compounds followed the order: NMP ≈ DMF > ACN. The percent removal for all the solvents tested followed the order: DBT > 4,6-DMDBT > TH. The diesel recovery of 95.8%, 96.2% and 98.6% was reported for NMP, DMF and ACN solvents, respectively. It is mentioned that recovery rates of diesel decrease significantly with increasing rate of desulfurization rates.

Extractive desulfurization of actual straight run gas oil (SRGO) was investigated by various researchers. Bailes (1981) investigated various organic solvents such as ACN, dimethyl sulfoxide (DMSO) and tetramethylene sulfone (sulfolane) for removal of sulfur and aromatic compounds from light oil using single stage solvent extraction at room T_E. It was mentioned that extraction equilibrium between extract and raffinate phases was achieved in 5 min or less and phases separation was achieved in about 10 s. ACN solvent was found to be suitable solvent for deep desulfurization of light distillates. Verduzco et al. (2004) studied the desulfurization of hydrotreated maxican SRGO (SC=320 ppmw; boiling range:200-345°C) with 2 ethoxyethenol ($C_4H_{10}O_2$), γ-butyrolactone ($C_4H_6O_2$), DMF, and ACN solvents in a glass batch reactor at T_E =25°C and S/F ratio of 1.0. Degree of sulfur removal depends on the nature of solvent and followed the order: DMF > $C_4H_{10}O_2 \approx C_4H_6O_2$ > ACN. Sampanthar et al. (2006) reported the capability of ACN, DMF, NMP and methanol solvents for desulfurization of real diesel (SC=430 ppmw) in the order: NMP > DMF > ACN > methanol.

In another work, Toteva et al. (2007) investigated the sulfur removal from lukoil unhydrotreated diesel using solvent extraction in a temperature controlled glass batch equilibrium extractor with DMF solvent at T_E of 90-120°C and S/F ratio ranging from 1 to 3.0. Sulfur reduced from 2.0 wt.% to 0.33 wt.% in two stage solvent extraction. Sulfur removal efficiency increased with an increase in S/F ratio whereas yield of desulfurized diesel decreased. Sulfur and aromatic removal efficiency of two stage extraction was found to be much higher than single stage. Reduction of sulfur content from 2.4 wt.% to less than 1 wt.% using single stage solvent extraction of Lukoil fuel oil with DMF and other solvents was also reported by Petkov et al. (2005). DMF was suggested as best solvent for sulfur removal from fuel oil among the acetone, methanol, and DMF solvents (Funakoshi, 1996).

Selectivity and capacity of a solvent can be adjusted to the great extent by adding the antisolvent which reduce the solvency power of main solvent or co solvent which increase solvency power of main solvent. Thus, addition of specific quantity of antisolvent and co-solvent in main solvent can adjust the selectivity and solvent power of the mixture to desired values. Gaile (2004) studied the solvent extractive refining of atmospheric gas oil (AGO) with 2-methoxyethanol (methyl cellosolve) and methyl cellosolve-water-pentane. Water and pentane with methyl cellosolve (MC) solvent were used as an antisolvent and as a co-solvent to improve the process efficiency. High process power consumption was noted as major drawback of extractive refining of AGO due to requirement of fairly high S/F and cosolvent to feed ratios of 5: 1 and 1: 1.5, respectively.

Abd-El-Aty et al. (2009) investigated the performance of NMP, DMF, DMSO and furfural solvents for solvent refining of diesel fuel fraction (boiling range: 212-343°C) obtained from the Suez oil petrochemical company. NMP and DMF solvents have low selectivity and high solvent power which can be modified by the addition of anti-solvent such as ethylene glycol , EG (Wauquier, 2000; Abd-El-Aty et al., 2009). EG was added to NMP and DMF to improve their solvent extraction performance. Extraction was carried out with DMSO, NMP and NMP+EG at T_E of 50°C and with furfural at 60°C. S/F ratio and EG content in NMP and DMF solvents were varied in the range of 1 to 5 wt.% and 5 to 20 wt.% respectively. Deceasing trend of miscibility temperature of various solvents (DMSO > furfural > DMF > NMP) indicates that DMSO has lowest solvent power (K), whereas NMP and DMF have the highest K, and furfural has medium value of K. It was observed that increase of S/F ratio lowers the raffinate yield but improves the raffinate quality by better removal of total aromatic and sulfur compounds and improving the diesel index. Trend of decrease in yield and improvement in the quality of raffinate for various solvent followed the order: DMSO > DMF+10 wt.% EG > furfural > NMP+10 wt.% EG. Sulfur content in raffinate varies in the range of 0.92 to 0.95 for nearly same raffinate yield (78 wt.%) when DMSO, NMP +10 wt.% EG and DMF + 10 wt.% EG were used at S/F ratio of 5.0, 1.2, 1.1 and 1.4, respectively. However, the raffinate yield varies in the range of 56.4 to 59.5 wt.% for raffinate sulfur content of approximately 0.6 when furfural, NMP + 10 wt.% EG and DMF + 10 wt.% EG solvents were used at the S/F ratio of 4.3, 3.2, and 4.3, respectively. It was observed that selectivity of DMSO is around five times than that of other solvents but its solvent power is lower by around 2 times. Authors correlated this finding to the high dielectric constant of DMSO (48.9) as compared to furfural (38), DMF (36.7), NMP (32.2) and EG (38.7). The effect of different selectivity and solvent power (K) of different solvents was observed on the yield and physical properties of raffinates obtained using the different S/F.

Countercurrent multistep solvent extraction with a set of temperature controlled funnels of three atmospheric gas oil samples having initial boiling point (IBP) and final boiling point (FBP) in the range of 278 to 397°C with NMP (BP=204)-undecane (BP=193°C) mixture was studied by Gail et al. (2006). Extraction was carried out with the aqueous NMP having 0.5 wt.% water at the S/F ratio in the range of 2-2.5, with undecane to feed weigh ratio in the range of 0.3-0.4 at the extractor top temperature of 30 and 40°C and bottom temperature at 30°C. NMP was found to have higher extraction efficiency for sulfur and aromatic compounds from gas oil with lower S/F ratio by 1.5 times than methyl cellosolve (MC). It was observed that addition of undecane to NMP increase the selectivity for removal of organosulfur sulfur and aromatic compounds. It was also mentioned that formation of azeotropic mixture (with boiling point 179°C) for undecane and NMP mixed solvent will lead to decrease in the regeneration temperature and probability of decomposition of NMP.

Performance of various aprotic and proton donor solvents was investigated for refining of diesel fraction generated from Uzbekistan crude’s rich in organic (sulfide) sulfur and sulfonable compounds (Gaile et al., 2010a). Aprotic solvents (ACN, DMF, DMA) and proton-donor solvents such as MC, tetrahydrofurfuryl alcohol (THFA), furfuryl alcohol (FA), and phenol along with water as anti-solvent and hexane as co-solvent were tested with diesel fraction in a temperature-controlled stirred separating funnel at temperature of 40°C and S/F weight ratio of 2:1 for removal of sulfur and aromatic compounds. Phenol + 3 wt.% water solvent was reported as best solvent with highest decrease in raffinate sulfur content from 2.02 to 0.9 wt.%. It was attributed to the high selectivity of phenol + 3% water solvent system to thiacyclanes organic sulfur compounds present in the majority in the South Uzbekistan crudes. Performance of aprotic solvents (DMF, DMAA) was found to be superior for removal of sulfonable compounds consisting of arenes and benzologs of thiophene but inferior for overall D_{sr} in comparison to phenol. Increases in raffinate yield and decreases in organic sulfur removal by 24.3 and 21.3, respectively, with increase in water content from 3 to 8 wt.% in the phenol were mentioned. Mixed solvent extraction reveals that additional of FA (50%) to phenol, further increase the raffinate yield by 31.1% but reduce the degree of sulfur removal by 24.3 wt.%. It was mentioned that DMF aprotic which are very effective for selective removal of aromatic and thiophenic sulfur compounds (polycyclic arenes; homologs of dibenzothiophene, benzothiophene, thiophene, thiazole, quinoline, carbazole) due to formation of fairly stable π complexes shows relatively poor performance in removal of organic sulfur compounds. Addition of hexane in phenol also results in more efficient extraction for improving the yield of raffinate. Authors also estimated the sulfur removal for multistep extraction using the Kremser equation. It was shown that removal of all sulfur compounds is possible using the 7 theoretical stages.

In another study, multi stage solvent extraction of high-sulfur diesel fraction of South Uzbekistan crudes rich in organic sulfur (70% of total sulfur) for removal of sulfur and aromatics compounds was reported by Gaile et al. (2010b). The multistep (seven) countercurrent extraction was represented by a system of temperature controlled separating funnels working as mixer-settler. Extraction was carried out with various solvents at different operation conditions of S/F weight ratio, water weight content in solvent (W_c), solvent-hexane mixture with specific hexane to feed weight ratio (H/F) and T_E. Details of extraction conditions with various solvents were DMF (S/F=3, W_c=4 wt.%), phenol (S/F=3, W_c=8 wt.%), DMF–hexane (S/F 5, H/F= 0.9, W_c=3 wt.% water), phenol-hexane (S/F=3, H/F=0.5; W_c=8 wt.%) at 50°C and FA (S/F=3, W_c=1 wt.%) at 60°C. Extraction performance of phenol + 8wt.% water and hexane solvent system was found to be more efficient than that of DMF and furfuryl alcohol. When this phenol solvent system was used in seven-step countercurrent extractive system at S/F weight ratio of 3.0 and H/F of 0.5, sulfur content reduced from 2.02

wt.% to 0.38 wt.% and sulfonable compounds reduced from 31.0 wt.% to 6.5 wt.% with an increase in the cetane index by 9 points at a raffinate yield of ~58.8 wt.%.

Petkov et al. (2004, 2005) investigated the effect of feed stock composition on extractive desulfurization performance. They studied the extractive desulfurization and dearomatization of heating gas oil (A=29.85; SC=0.47%) and hydrotreated middle distillate (A=27.1; SC=0.2%) using selective solvents like methanol at 20, 30 and 50°C, furfural at 60 and 80°C and EG at 50 and 90°C and 40% NaOH in methanol at 50 and 90°C, using S/F ratio in the range of 0.5 to 2.0. Percent sulfur removal increased with an increase in T_E and S/F ratio. Among all tested solvents, furfural was reported to be most efficient solvent. It was shown that the sulfur and aromatic content of hydrotreated middle distillate can be reduced by 7 fold (from 0.2 to 0.029 wt.%) and 3 folds (from 27.1 to 8%), respectively using the solvent extraction with methanol, furfural, and EG whereas for heating oil, these values of sulfur and aromatic reduction are 5 and 1.6 folds, respectively, under the operating conditions used in the study. Significantly different desulfurization efficiency for heating gas oil and hydrotreated middle distillate was attributed to the different nature of middle distillate fractions. Presence of higher nonaromatic sulfur compounds in heating gas oil than that of hydrotreated diesel may be reason for lower sulfur removal efficiency, but for understanding the lower aromatic removal efficiency, need of additional exploration was suggested.

An optimization of operating conditions was carried out for solvent refining of middle distillate fraction with furfural solvent for removal of sulfur and polyaromatics by Yordanov et al. (2009). Fractional factorial design was used to estimate the corresponding values of independent variables for carrying out the experimental runs (2^{N-1}) required for optimization method. The selected value of lower and upper limit for independent variables such as time of reaction, T_E, S/F ratio and rate of agitation time were 60-120 min, 30-60°C, 1-3 and 1-2 sec^{-1}, respectively. Box-Wilson method was used for obtaining the optimized values of independent variables. At the optimized operating conditions, the raffinate contained 47.5 ppmw sulfur and 0.51 wt.% polycyclic aromatics. Time of reaction and agitation time were found the most important independent factors affecting the sulfur content in raffinate. It is to be noted that S/F is generally the most significant parameter which affects the removal of impurities. However, higher significance of time of reaction and agitation time in this study may be attributed to the narrow range and absolute value of agitation rate (60-120 rpm) selected.

Application of construction and calculated methods (Treybal, 1963) in solvent refining of gas oil was demonstrated by Hassan et al. (2009). They generated the countercurrent extraction results using the liquid-liquid equilibrium data ternary diagrams of diesel with various solvent (Abd-El-Aty et al., 2009). Number of theoretical stages required to produce the raffinate and extract phases using appropriate S/F were estimated using ternary equilibrium diagram based graphical (difference point) method (Treybal, 1963). Minimum and maximum amount of solvents for generating the final raffinate and extract and appropriate amount of solvent to produce raffinate and extract were estimated. It was mentioned that appropriate S/F ratio are 17.4, 1.1, 0.78 and 1.15 for DMSO, furfural, NMP+10 wt.% EG and DMF + 10 wt.% EG, respectively. The number of stages varies between 14 and 8 at S/F depending upon the solvent. DMSO was found to be very selective solvent and generated raffinate containing higher aromatics of 11.3 wt.% and sulfur of 0.62 wt.% with higher raffinate yield of 76.7 wt.% at S/F 17.4 with 14 stages. DMF+10wt.% EG was found to be the best solvent to produces raffinate with least aromatics (5.4 wt.%) and sulfur contents (0.32 wt.%) and best yield with best extract purity in comparison to furfural and NMP + 10 wt.% EG at same S/F ratio and with few more stages. Though, DMSO has highest selectivity, still it is not recommended as the best solvent due to requirement of high operating cost and big size of most of the equipments due to the need of high S/F ratio. In view of higher thermal stability and lower corrosive nature, NMP + 10wt.% EG was proposed for considering as a promising solvent mixture for extraction of diesel fraction. This solvent produced the raffinate containing sulfur and aromatics content of 0.41 and 7.1 wt.% with yield of 68.6 wt.% and extracts of 78.4 wt.% aromatics purity at S/F of 1.1 and 6 theoretical stages.

Summary of the experimental studies for sulfur removal from synthetic diesel and real gas oils using organic solvents without and with co/anti-solvents has been tabulated in Table 2.1, 2.2 and 2.3, respectively.

Table 2.1. Comparative analysis of solvent extraction of model sulfur compounds from synthetic diesel.

Feedstock (F)	Solvent (S)	S/F	T_E (°C)	No. of stages	R-yield	R-Sulfur (ppmw	Reference
2-MT+ hexadecane (S=847)	ACN	1.0	60	Single	-	822	Caero et al . 2005
2,5-DMT+ hexadecane (SC=720)						714	
BT+ hexadecane (SC=612)						587	
DBT +hexadecane (SC=445)						433	
4-MDBT+hexadecane (SC=414)						408	
4,6-DMDBT +hexadecane (SC=387)						383	
Synthetic diesel (SC=600 ppmw) (T, BT and 4,6 DMBDT+N-octane)	ACN	0.2	29	Single	98.6	523	Bakara, 2012
	DMF				96.2	437	
	NMP				95.8	435	

R=raffinate; T_E=Extraction temperature; T=thiophene; 2-MT=2-methylthiophene; 2,5-DMT=2,5-dimethylthiophene; BT=Benzothiophene; DBT=dibenzothiophene; 4-MDBT=4-dimethyldibenzothiophene; 4,6-DMDBT=4,6-dimethyldibenzothiophene; ACN=Acetonitrile; DMF=N,N-Dimethylformamide; NMP=*N*-methylpyrrolidone

Table 2.2. Comparative analysis of solvent extraction of sulfur compounds from gas oil using various organic solvents.

Feedstock (F)	Solvent (S)	S/F or recycled S/F	T_E (°C)	Batch (B)/ Contin-uous (C	No. of stage	R-yield	R-Sulfur (ppmw/ wt.%)	Reference
Hydrotreated Maxican SRGO (SC=320 ppmw; IBP/FBP=200/345°C)	ACN,	1	25	B	1	-	220	Verduzco et al 2004
	DMF						130	
	$C_4H_{10}O_2$,						180	
	$C_4H_6O_2$						180	
Real diesel (SC=430 ppmw)	ACN	0.4	-	B	1	-	310	Sampanthar et al 2006
	Methanol.	1.0					314	
	DMF	0.4					226	
	NMP	0.4					219	
SRGO (SC=1.35 wt.%)	ACN	1.0	-	B	1	*96.2*	1.13	Shujiro Otsuki et al. 2000
	Methanol.					*95.8*	1.13	
	DMSO					*95.4*	1.06	
	Sulfolane					*96.0*	1.08	
	DMF					*88.2*	0.57	
VGO (SC=2.17 wt.%)	ACN	1	50	B	1	*99.8*	2.44	Shujiro Otsuki et al. 2000
		1.5			10	*78.0*	1.45	
	Methanol.	1			1	*99.8*	2.06	
		1.5			10	*68.0*	1.76	
Diesel (SC=1.566 wt.%; A=29.5 wt.%	DMSO	3	50	B	1	*84.0*	0.9804	Hassan et al., 2013.

A=Aromatics; SC=Sulfur content; R=raffinate; VGO=Vacuum gas oil; SRGO=Straight run light gas oil; ACN=Acetonitrile; DMF=N,N-dimethylformamide; DMSO=Dimethyl sulfoxide; Sulfolane=Tetramethylene sulfones; EG=Ethylene glycol; NMP=*N*-methylpyrrolidone; $C_4H_{10}O_2$=2-ethoxyethenol; $C_4H_6O_2$=γ-butyrolactone; ## Estimated stages.

Table 2.2 continued

Feedstock (F)	Solvent (S)	S/F or recycled S/F	T_E (°C)	Batch (B)/ Contin- uous (C	No. of stage	R-yield	R-Sulfur (ppmw or wt.%)	Reference
Heating gas oil (A=29.85; SC=0.47 wt.%)	Methanol	0.5-2.0	20, 30, 50	B	1	82.7	0.16	Petkov et al. 2004
	Furfural		60, 80			80.8	0.09	
	EG		50, 90			81.3	.19	
Hydrotreated middle distillate (A=27.1; SC=0.2 wt.%)	Methanol	0.5-2.0	20, 30, 50	B	1	72.4	0.035	Petkov et al. 2004
	Furfural		60, 80			86.9	0.0288	
	EG		50, 90			86.5	0.041	
	40% NaOH in methanol		50, 90			0.08	80.2	
Lukoil unhydrotreated diesel (SC=2.0%)	DMF	0.5-3.0	90,120	B	1	69.1	-	Toteva and Topalova 2007
		1.0-3.0	90,120		1	41.4	0.33	
Diesel fraction (SC=1.5667, A=29.5)	DMSO,	5.0	50	B	1	78.0	0.921	Abd-El-Aty et al., 2009
	Furfural	1.2	60			78.0	0.950	
		4.3				55.4	~0.6	
Diesel fraction (SC=1.5667, A=29.5)	DMSO	17.4	50	-	$14^{\#\#}$	76.7	0.62	Hassan et al., 2009
	Furfural	1.1	50		$8^{\#\#}$	67.9	0.35	

A=Aromatics; SC=Sulfur content; R=raffinate; DMF=N,N-Dimethylformamide; DMSO=Dimethyl sulfoxide; EG=Ethylene glycol; ## Estimated no of stages using LLE data

Table 2.3. Comparative analysis of solvent extraction of sulfur compounds from gas oil using various organic solvents along with co/anti –solvents.

Feedstock (F)	Solvent (S)	Co-solvent (CS)	Water/ Anti-solvent (AS)	S/F or recycled S/F ratio	CS/F ratio	Water/AS (%)	T_E (°C)	Batch (B)/Continuous (C)	No. of Stages	R-yield	R-Sulfur (wt.%)	Reference
Diesel fraction of South Uzbekistan crude (SC=2.02)	ACN	-	Water	3.0	-	3.0			1	74.5	1.321	Gaile et al., 2010a
	MC									85.9	1.707	
	DMF									74.7	1.139	
	DMAA									74.4	1.101	
	THFA									84.2	1.329	
	DMF-THFA									80.7	1.260	
	Phenol									48.3	0.400	
	FA					8.0				84.4	1.190	
	FA + phenol (50/50)					3.0				78.8	0.891	

A=Aromatics; SC=Sulfur content; AS=Anti-solvent; R=raffinate; ACN=Acetonitrile; DMF=N,N-Dimethylformamide; MC=Methyl Cellosolve; DMAA=Dimethylacetamide; THFA=Tetrahydrofurfuryl alcohol; FA=Furfuryl alcohol.

Table 2.3 continued

Feedstock (F)	Solvent (S)	Co-solvent (CS)	Water/ (AS)	S/F or recycled S/F ratio	CS/F ratio	Water/AS (%)	T_E (°C)	Batch (B)/Continuous (C)	No. of Stages	R-yield	R-Sulfur (wt.%)	Reference
Diesel fraction of South Uzbekistan crude (SC=2.02)	ACN	Hexane	Water	3.0	1.0	3.0	40	B	1	80.7	1.400	Gaile et al., 2010a
	MC									88.7	1.749	
	DMF									80.9	1.321	
	DMAA									80.2	1.339	
	THFA									86.4	1.380	
	DMF-THFA									85.2	1.440	
	Phenol									65.0	0.620	
	FA									88.0	1.301	

A=Aromatics; SC=Sulfur content; AS=Anti-solvent; R=raffinate; ACN=Acetonitrile; DMF=N,N-Dimethylformamide; MC=Methyl Cellosolve; DMAA=Dimethylacetamide; THFA=Tetrahydrofurfuryl alcohol; FA=Furfuryl alcohol.

Table 2.3 continued

Feedstock (F)	Solvent (S)	Co-solvent (CS)	Water/ Anti-solvent (AS)	S/F or recycled S/F ratio	CS/F ratio	Water/AS (%)	T_E (°C)	Batch (B)/Con-tinuous (C)	No. of Stages	R-yield	R-Sulfur (wt.%)	Reference
AGO-I (SC=1.13 IBP/90%=279/ 266)	NMP		Water	2.0	-	0.5	TT-40 BT-30	C	4[#]	75.1	0.40	Gail et al.,2006
	MC	---	Water	3.0	-	4.0	TT-30 BT-30	C	5[#]	80.5	0.74	
AGO-II (SC=1.15 IBP/90%=278/ 284)	NMP	undecane	Water	2.0	0.3	0.5	TT-40 BT-30	C	4[#]	77.6	0.47	
AGO-III (SC=1.17 IBP/90%=290/ 297)	NMP	undecane	Water	2.5	0.4	0.5	TT-40 BT-30	C	4[#]	75.0	NR	
Diesel fraction of South Uzbekistan crude (SC=2.02)	Phenol	-	Water	3.0	-	-	-	-	7[##]	-	zero	Gaile et al., 2010a
	FA	-		8.0	-	-	-	-	7[##]		0.606	
	Phenol	Hexane	Water	3	1.0	3.0	40	B	7[##]	-	0.004	
	DMMA	Hexane	Water	3	1.0	3.0	40	[#]C	7[##]		0.6464	

SC=Sulfur content; AS=Anti-solvent; R=raffinate; AGO=Atmoshpheric gas oil; NMP=*N*-methylpyrrolidone; MC=Methyl Cellosolve; DMAA=Dimethylacetamide; FA=Furfuryl alcohol; [#]Multi stages counter current extraction using temperature controlled separating funnels (TCSF); [##]Estimated no. of stages using LLE data; TT=top temperature; BT=bottom temperature.

Table 2.3 continued

Feedstock (F)	Solvent (S)	Co-solvent (CS)	Water/ Anti-solvent (AS)	S/F or recycled S/F ratio	CS/F ratio	Water /AS (%)	T_E (°C)	Batch (B) / Continuous (C)	No. of Stages	R-yield	R-Sulfur (wt.%)	Reference
Diesel fraction of South Uzbekistan crude (SC=2.02)	DMF	-	Water	3.0	-	4	50	C	$7^{\#}$	64.97	0.83	Gaile et al., 2010b
	DMF	Hexane	Water	5	0.9	3	50		$7^{\#}$	70.53	0.89	
	Phenol	-	Water	3.0	-	8	50		$7^{\#}$	45.8	0.23	
	Phenol	Hexane	Water	3.0	0.5	8	50		$7^{\#}$	58.8	0.38	
	FA		Water	3.0	-	1	60		$7^{\#}$	63.9	0.90	
Diesel fraction (SC=1.5667, A=29.5)	DMF	-	EG	1.4	-	10	50	B	1	~78.0	0.94	Abd El-Aty,2009
	NMP	-	EG	1.1	-	10	50		1	~78.0	0.92	
Diesel fraction (SC=1.5667, A=29.5)	NMP	-	EG	0.78	-	10	50	-	-	69.6	0.41	Hassan et al., 2009
	DMF	-	EG	1.15	-	10	50	-	$13^{\#\#}$	69.8	0.32	

A=Aromatics; SC=Sulfur content; R=raffinate; DMF=N,N-Dimethylformamide; NMP=*N*-methylpyrrolidone; MC=Methyl Cellosolve; FA=Furfuryl alcohol; EG=Ethylene glycol; $^{\#}$Multi stages counter current extraction using temperature controlled separating funnels (TCSF);, $^{\#\#}$ Estimated no of stages using LLE data.

2.4.1.2. Ionic liquid solvents

ILs were reported as suitable alternative to organic solvents for removal of refractive aromatic sulfur compounds due to their various eye-catching properties such as chemical and thermal stability, nonflammability, non-volatility and environmentally friendly due to their very low vapor pressure (Nie et al., 2006; Varma et al., 2011). Moreover, chemical and physical properties of ILs heavily depend on their cation and anion combination. A number of cations and anions have been reported in literature with various possible combinations can generate a range of ILs. This facilitates the design of novel liquid–liquid extraction systems using tailored ILs to perform selective impurity separations. Various studies have focused on the removal of thiophene sulfur compounds from model oil such as n-hexane, octane, toluene, cyclohenxane, etc. and desulfurization of synthetic diesel prepared by adding the model compounds which are generally present in gas oil using ILs (Alonso et al., 2007; ; Kumar and Banerjee, 2009: Francisco et al., 2010; Arce et al., 2010; Verma et al., 2011; Anantharaj and Banerjee, 2011a,b).

An experimental investigation of thiophene removal from aliphatic hydrocarbon (ioctane) was studied using ionic liquid [OMIM][BF4]. High solubility of thiophene in the IL phase and high selectivity of ILs up to 27.62 was found. In view of these results, it was mentioned that aromatic sulfur compounds have high affinity with ILs (Arce et al., 2008a; Arce et al., 2008b; Kumar and Banerjee, 2009; Arce et al., 2010). EBer et al (2004) investigated the ILs made of an alkyl substituted imidazolium group as cation and various anions for removal of thiophene and its derivatives from the synthetic fuels. Zhang et al. (2004) reported a comprehensive study for evaluation of alkylimidazolium-based ILs with BF_4 and PF_6 as the anions for desulfurization purpose. An improvement in extraction performance was reported with PF_6 anion. Holbrey et al. (2008) investigated a range of ILs using the various cation and anion combination for DBT extraction from dodecane. It was found that polyaromatic quinolinum-based ionic liquids showed best extractive ability, but high melting points of polyaromatics cations such as 1,3-dibenzimidazolium restricts their utilization. This study ranks ionic liquid desulfurization ability with respect to cation in order: methylpiridinium ≥ yridinium ≈ imidazolium ≈ pyrrolidinium. It is mentioned that the effect of variation in anion type on desulfurization is marginal. Performance of phosphoric acids based ILs (1 methyl-3-methylimidazolium dimethylphosphate ([MMIM][DMP]), 1-ethyl-3-methylimidazolium diethylphosphate ([EMIM][DEP]), and 1-butyl-3-methylimidazolim dibutyl phosphate ([BMIM][DBP]) was also investigated for removal of thiophenic sulfur compounds (3-MBT, BT, DBT) from synthetic diesel (Kumar and Banerjee, 2009). Application of pyridinium ILs as a potential solvents for deep sulfur removal using multiple extraction cycles was shown by Wang et al. (2007).

Various aspects of extractive desulfurization of fuel oil using ILs along with comprehensive discussions on various factors such as type of ILs species, T_E and extraction time, S/F ratio, feed species, initial sulfur content, solvent regeneration as well as potential problems in their application which control their performance and industrial application in extractive desulfurization have been reported in the recently published review articles (Kulkarni and Afonso, 2010; Dharaskar, 2012; Rashid et al., 2014).

2.3. SOLVENT EXTRACTIVE DESULFURIZATION OF OXIDIZED GAS OIL

SEDS is based on the different distribution of sulfur compounds between the oil rich raffinate and the solvent rich extract phase due to difference in the polarity of sulfur and other gas oil compounds. Polarity difference in sulfur and aromatic compounds of gas oil is not very high. The polarity of the sulfur compounds can be increased by their oxidation to sulfones. Thus, oxidation enhances sulfur compounds selectivity and solubility in the solvents which results in improved D_{sr} and minimizes the loss of diesel product at the expense of additional step of oxidation and recovery of unused oxidant and catalyst (homogeneous) and consumption of expensive oxidants. Organic and ILs both type of solvents have been studied for separation of sulfones from oxidized diesel. Some of the studies on solvent extraction of sulfones from oxidized gas oil is discussed and reviewed in this section.

Otsuki et al. (2000) demonstrated the effect of oxidation on improvement in the sulfur removal efficiency. They studied the extraction of unoxidized (SC=1.35 wt.%) and oxidized (SC=0.65 wt.%) straight run light gas oil (SRLGO) and vacuum gas oil (VGO) with various organic solvents such as DMF, ACN, methanol, DMSO, and sulfolane at S/F ratio of 1.0. Sulfur content (SC) in the product obtained from extraction of oxidized and unoxidized SRLGO was in the range of 0.10-0.18 wt.% and 0.57-1.13 wt.%, respectively. Product recoveries from oxidized SRLGO were lower by 1.2-6.1% in comparison to unoxidized SRLGO, depending up on the solvent used. For unoxidised SRLGO, DMF solvent gives highest sulfur removal of 57.7% in comparison to solvents which gives sulfur removal in the range of 16-22%. Difference in sulfur removal efficiency of all solvents from oxidized SR-LGO was found to be marginal. Sulfur content in the oil phase obtained from the extraction of oxidized VGO was 1.09, 1.67 and 0.41wt.%, respectively for ACN, methanol, and DMF solvents. Thus, for solvent extraction of oxidized VGO (SC=1.48wt.%), the sulfur removal efficiency of DMF was found to be 2.66 fold of ACN in single stage and 12 folds in multistage extraction. It was also found that yield of oil phases decreases in every stage of multistage extraction to the minimum value of around 40% for DMF solvent.

Shiraishi et al. (2002) reported oxidative desulfurization of light gas oil (LGO), commercial light oil (CLO) and light cycle oil (LCO) using ACN-water mixture

(ACN/Water=84/16). Solvent was used along with feed, oxidant, and catalyst in the reaction vessel. Raffinate and extract phase were separated by providing the sufficient settling time after completion of oxidation reaction. D_{sr} followed the order: LGO > CLO > LCO. This order is same as that of aromatic concentration in these oils. This suggests that extractability of the sulfones from gas oil is affected by its aromatic content adversely. The yield of desulfurized oils increases with an increase in W_c in ACN. It was observed that extractability of sulfones of DBTs and BTs become easier with increase in the length or number of alkyl substituents. Extractability of sulfones depends on the dipole moment values for the compounds. For sulfones of alkylated DBT, dipole moment decrease till two carbon numbers of alkyl groups and then increase. Dipole moment values for sulfones of BT increases with an increase in the carbon number of substituted alky group. In this study, values of dipole moment and extractability of sulfones were correlated. It was found that that higher dipole moment values were responsible for easy extraction of highly substituted sulfones (Zannikos et al., 1995).

Verduzco et al. (2004) evaluated the performance of various solvents like 2- $C_4H_{10}O_2$, $C_4H_6O_2$, DMF, and ACN solvents for oxidative desulfurization of hydrotreated maxican SRGO (SC=320 ppmw; boiling range: 200-345°C) using the S/F of 1.0. Sulfur removal efficiency of solvent followed the order $C_4H_{10}O_2 > \text{DMF} \approx C_4H_6O_2 > \text{ACN}$. It was mentioned that sulfur removal efficiency of solvents for extractive desulfurization followed the order: $\text{DMF} > C_4H_{10}O_2 >\approx C_4H_6O_2 > \text{ACN}$. It was observed that tough total removal of sulfur using the DMF and $C_4H_6O_2$ solvents is comparable but removal 4, 6 DMDBT is 1.7 times higher for $C_4H_6O_2$ than DMF and removal of 4, 6, 9 TMDBT is 1.6 times higher for DMF than $C_4H_6O_2$. This suggests that there is a synergism between catalyst, extraction solvent and structure of sulfur compounds.

Sampanthar et al. (2006) reported of oxidative desulfurization of synthetic diesel (SC=600 ppmw). Diesel was prepared by adding the equimolar amount of 4-MDBT, 4,6-DMDBT, and 4,6-DEDBT in n-tetradecane. Solvent extraction of real diesel was carried out using polar solvents like ACN, DMF, NMP and methanol. The solvent extraction performance for unoxidzed real diesel was found in order NMP > DMF > ACN > methanol. Solvent refining of oxidized diesel (SC=430 ppmw) was carried out using ACN, DMF, NMP and methanol. NMP was found to be more efficient than DMF.

Extractive removal of sulfones from oxidized diesel (A=15.9 wt.%; SC=0.5691 wt.%) using DMSO solvent is also reported by Hassan et al (2013). Extraction of oxidized diesel was carried out in a mixer-settler at the controlled temperature of 50°C, using the string time of 45 min, settling time of 45 min for phase separation with S/F ratio in the range of 1-5. Generated phase equilibrium data and ternary miscibility diagram were used for understanding the solvent solubility in the raffinate hydrocarbon, solvent selectivity, product purity and estimation of theoretical stages for counter current solvent extraction system. Decrease in SC and yield of raffinate with increase in S/F was observed. It is mentioned that application of maximum quantity of solvent (S_{max}) would yield a raffinate phase rich in nonaromatics hydrocarbons whereas minimum quantity (S_{min}) of solvent yields a extract phase rich in aromatic hydrocarbons. Thus, medium amount of solvent in the range of S_{min}-S_{max} in actual continuous extraction process will provide the raffinate and the extract phases of desired purity. It was found that raffinate with sulfur of 0.0224 wt.% can be produced with DMSO solvent using various S/F ratios of 1, 1.5, 2 and 3/1 with the corresponding theoretical stages of >8, 4, 3, and 2 with the respective raffinate yield of 84.9%, 84.2%, 83.6% and 82.8%. This reveals that requirement of theoretical stages can be reduced by using high S/F with slight penalty on raffinate yield. A comparative analysis of sulfur removal from oxidized gas oil is given in Table 2.4.

2.4. DISPOSAL AND UTILIZATION OF EXTRACT HYDROCARBON

It is known that the major disadvantage of extractive desulfurization of gas oil is loss of desired hydrocarbon with removed sulfur compounds. This loss can be minimized and aromatic concentration in extract can be increased by using the solvent of proper capacity and selectivity and application of co/anti solvent along with optimized T_E and S/F ratio. Further, extract rich in aromatic hydrocarbons can be utilized as product to make this process more economical. It is reported that extract can find its efficient use for removal of asphaltene–resin–paraffin deposits in oil production and in production of technical detergents (Gail et al., 2010b). Moreover, extract rich in dicyclic and polycyclic aromatics compounds can be used as a rubber solvent, a reactor coolant in atomic power generation and as a feed stock to carbon generation unit. The dicyclic aromatic rich extract can also be used naphthalene production by hydrodealkylation (Hassan et al., 2013).

Table 2.4. Comparative analysis of extraction of sulfones from oxidized gas oils using organic solvents.

Feedstock (F)	Solvent (S)	S/F	T_E (°C)	No. of stages	R-yield	R-Sulfur (ppmw/ wt.%)	Reference
Oxidized SRGO (S=0.65 wt.%)	ACN	1.0	*RT*	1	90.1	0.10	Otsuki et al., 2000
	Methanol				90.5	0.18	
	DMSO				91.1	0.11	
	Sulfolane				94.8	0.12	
	DMF				85.9	0.11	
Oxidized Vacuum gas oil (S=1.48%)	ACN	1.0	*RT*	1	92.5	1.09	Otsuki et al., 2000
				10	55.0	0.12	
	Methanol			1	96.0	1.67	
				10	66.0	.21	
	DMF			1	80.0	0.41	
				10	40.0	0.01	
Hydrotreated Maxican SRGO (S=320 ppmw; IBP/FBP=200/345)	ACN	1.0	-	1	-	140	Verduzco et al 2004
	DMF					124	
	$C_4H_{10}O_2$,					130	
	$C_4H_6O_2$					90	
Oxidized diesel (S=430 ppmw)	ACN	0.4	-	1	-	198	Sampanthar et al., 2006
	Methanol	1				172	
	DMF	0.4				117	
	NMP	0.4				108	
Oxidized diesel (S=0.5691 wt.%; A=15.9 wt.%)	DMSO	1.1	50	$>8^{\#\#}$	84.9	0.0224	Hassan et al., 2013.
		1.5		$4^{\#\#}$	84.18	0.0224	
		2.0		$3^{\#\#}$	83.6	0.0224	
		3.0		$2^{\#\#}$	82.8	0.0224	

A=Aromatics; SC=Sulfur content; ACN=Acetonitrile; DMF=N,N-Dimethylformamide; DMSO=Dimethyl sulfoxide; Sulfolane=Tetramethylene sulfones; NMP=*N*-methylpyrrolidone; $C_4H_{10}O_2$=2-ethoxyethenol; $C_4H_6O_2$=γ-butyrolactone; DMAA=Dimethylacetamide; ##Number of stages estimated using LLE data.

EVALUATION OF SOLVENTS

3.1. GENERAL

Literature review (as given in chapter 2) shows that no comprehensive strategy is reported in the literature on solvent evaluation for desulfurization and denitrification. Considering this research gap, a new strategy for a realistic and practical screening of solvents for removal of highly refractory sulfur and nitrogen compounds from gas oil has been evolved (Figure 3.1) and presented in this study. Two major class of solvents vis-a-vis conventional organic solvents and ionic liquid solvents (ILs) are used for aromatic, sulfur and nitrogen compounds removal from hydrocarbon streams (Alonso et al., Gao et al., 2013; Gaile et al., 2010a,b; 2007; Shiraishi et al., 2002; Petkov et al., 2004; Hassan et al., 2009). Six most widely used industrially proven conventional organic solvents and twenty two imidazolium based IL solvents were selected for removal of benzothiophene (BT), dibenzothiophene (DBT) and their alkylated devrivatives, and nitrogen compounds from gas oil. The solubility parameters, molar volume, van der waals volume of sulfur, aromatics and nitrogen compounds which can represent the gas oil were estimated using ab initio molecular dynamics method using commercial softwares. These parameters were used for estimating the standard heat of vaporization which is of immense interest to the researchers and have not been reported in the literature and activity coefficients at infinite dilution of model gas oil compounds in solvents using available correlations. The capacity, selectivity and performance index (P_I) of solvents were estimated for selected sulfur and nitrogen compounds. To understand the effect of complexity of solvent recovery section on their industrial utilization, two type of solvent recovery sections were conceptualized for recovering of solvents: one having boiling point lower than gas oil and the other for solvents having boiling point in the range gas oil distillation. Based on complexity of recovery section, a new industrial usability index (S_{IUI}) of solvent was defined and used for their rating for sulfur and nitrogen compounds from gas oil.

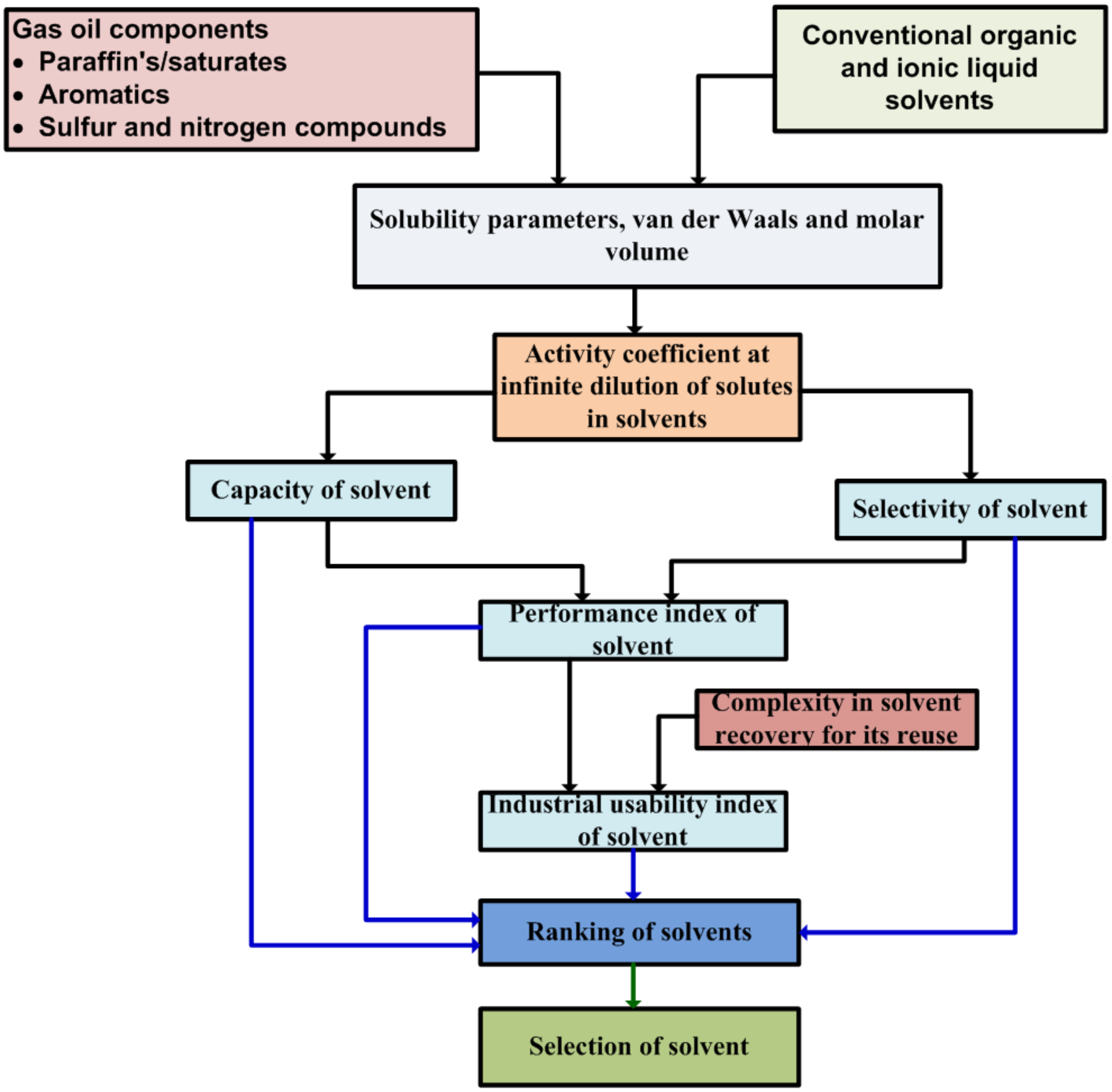


Figure 3.1. Schematic of strategy for evaluation of solvents for sulfur and nitrogen compounds removal from gas oil.

3.2. THEORY

3.2.1. Solubility Parameters, Activity Coefficient at Infinite Dilution, Capacity and Selectivity of Solvents

The Hildebrand solubility parameter (δ) is derived from the cohesive energy density of the compound, which in turn is derived from the heat of vaporization (Derecskei and Kovacs, 2008; Hansen, 1967):

$$\delta = \sqrt{\Delta E_{ced}} = \left[\frac{\Delta H_v - RT}{V_m} \right]^{1/2} \tag{3.1}$$

where, δ is the Hildebrand solubility parameter; ΔE_{ced} is the cohesive energy density; ΔH_v is the enthalpy of vaporization; R is the universal gas constant; T is the absolute temperature and V_m is the molar volume.

Activity coefficient at infinite dilution of solute in solvents (γ_i^{∞})plays an important role in understanding of solvent extraction process. The correlation of the activity coefficients at infinite dilution is represented by a two-term equation (Wang et al., 2013).

$$\ln \gamma_i^{\infty} = \ln \gamma_i^{\infty comb} + \ln \gamma_i^{\infty res} = \ln\left(\frac{r_{vwdi}}{r_{vwds}}\right)^{2/3} + 1 - \left(\frac{r_{vwdi}}{r_{vwds}}\right)^{2/3} + \left(\frac{V_{mi}}{RT}\right)(\delta_i - \delta_s)^2 \tag{3.2}$$

where, r_{vwdi} represents van der Waals volume of solute, r_{vwds} represents van der Waals volume of solvent, V_{mi} represents molar volume of solute and δ represents solubility parameters.

Capacity (or loading capacity) of the solvent (C_i) means the maximum concentration of solute that a solvent can contain under specified conditions. The capacity signifies the ability of solvent to dissolve maximum amount of solute (Anantharaj and Banerjee, 2011b). It can be defined in term of activity coefficient at infinite dilution as (Anantharaj and Banerjee, 2011a):

$$\text{Capacity of solvent } (C_i) = \frac{\text{Amount of desired impurities removed}}{\text{Amount of solvent}} = \frac{1}{\gamma^{\infty}_{isp}} \tag{3.3}$$

where, i, sp and γ_i^{∞} denote the solute name, solvent rich phase, and activity coefficients at infinite dilution.

The selectivity of solvent (S_{ij}) shows the tendency of component i to be extracted more readily from carrier phase to solvent phase than component j. It is defined as the ratio of the composition (mole/weight fraction) of solute (sulfur and nitrogen compounds) in the extract rich solvent phase and its composition in raffinate (gas oil) phase. For liquid-liquid extraction process, it can be defined as the ratio of distribution coefficients of components i and j. It is important to mention that if the solvent employed is not very soluble in feed phase, the activity coefficients of components i and j in carrier phase will be nearly independent of the nature of the solvent. The selectivity of the solvent for solute i with respect to solute j can be expressed using the following equation (Anantharaj and Banerjee, 2011a):

$$Selectivity = S_{ij} = \left(\frac{\gamma^{\infty}{}_{jsp}}{\gamma^{\infty}{}_{isp}}\right)^{\text{extract phase}} \left(\frac{\gamma^{\infty}{}_{jsp}}{\gamma^{\infty}{}_{isp}}\right)^{\text{raffinate phase}} = \left(\frac{\gamma^{\infty}{}_{jsp}}{\gamma^{\infty}{}_{isp}}\right)^{\text{extract phase}} \approx \frac{\gamma^{\infty}{}_{jsp}}{\gamma^{\infty}{}_{isp}} \quad (3.4)$$

Here, subscript '*i*' refers to the sulfur or nitrogen compounds which are to be removed and subscript '*j*' refers to the gas-oil component. Similarly, yield is defined as:

$$\text{Yield}=\frac{\text{Amount of product }\left(\text{solvent free raffinate phase}\right)\text{obtained after extraction}}{\text{Amount of feed (without solvent)}} \quad (3.\ 5)$$

3.2.2. Performance Index (P_I) of Solvents

Capacity and selectivity properties of solvent are among the most desired properties. These have been used for screening of solvents for separation of particular compounds (Anantharaj and Banerjee, 2011a,b; Song et al., 2006; Wang et al., 2013). From the economic point of view, maximization of desulfurized gas oil yield and impurities removal is desired during solvent extraction process for removal of sulfur, nitrogen and polyaromatics from gas oil. Higher capacity of solvent leads to higher removal of impurities and lower yield of product. This suggests that solvent having higher capacity will result in more loss of desired product with extract, however, requires lower solvent to feed ratio (S/F) for same extent of impurities removal. Further, higher selectivity of solvent in gas-oil extraction (tendency of undesired component such as sulfur and nitrogen compounds to be extracted more readily from carrier phase to solvent phase than desired compound such as paraffins) will reduce the loss of desired material with extract but require large amount of solvent for impurities removal. Among, capacity and selectivity, capacity is more important for the selection of an optimum extraction process as it determines the flow rate of the circulating solvent, which in turn governs the size of the reactor and capital and operating cost. However, selectivity is also an important parameter in solvent evaluation. Since, highly selective solvents generally have lower capacity or dissolving power, therefore, large amount of solvent required increases the plant size and operational cost of extraction and solvent recovery equipments. In view of contradictory benefits of these two properties in solvent extraction, the balance of these properties in the solvent is preferred. Therefore, the effect of these two important parameters has been combined in single factor called as P_I to guide us to select a solvent which has moderate capacity and solubility for an economical solvent extraction process. P_I is defined as (Kumar and Banerjee, 2009):

$$P_I = C_i S_{ij} \tag{3.6}$$

3.2.3. Industrial Usability Index (S_{IUI})

In commercial extraction process, solvent is re-circulated via its recovery from extract and raffinate phase. Therefore, the economics of the process is greatly governed by the energy requirement, complexity of solvent recovery section and capital investment required for solvent recovery. This may be the reason that solvent showing the best capacity and selectivity in the laboratory scale could not be commercialized in the industry. In view of the above, it is essential to integrate above factors with P_I of solvent for a realistic screening of solvents for a given separation.

The complexity of design of solvent recovery section largely depends on boiling point difference between solvent and feed. In processes where boiling point of gas oil is 50°C or more above than that of solvent, the solvent recovery is possible using the process design as shown in Figure 3.2. The feed and solvent come in contact in counter current fashion in an extractor where raffinate and extract phases get generated. The solvent from raffinate phase is removed in raffinate wash column (RWC) using water. The extract phase is fed to solvent recovery column (SRC) where solvent is vaporized and recovered from the top. The aqueous solvent obtained from RWC and SRC is processed in solvent drying column (SDC) to remove the excess water. The solvent from SDC bottom is sent to the extractor column after recovering its heat in the process. The water vapor from drying column can be partially condensed to meet the requirement of RWC and rest vapor can be superheated for use as stripping steam in SRC.

Further, in the scenario where boiling point of solvent (for most of ILs) is more than that of gas oil or where difference between solvent and gas oil is either not sufficient or has boiling point overlap, highly complicated solvent recovery section with additional secondary solvent is required as shown in Figure 3.3. In this process, extraction and solvent removal from raffinate phase is similar as described above (Figure 3.2). The extract phase is routed to re-extraction column where low boiling hydrocarbon (LBH) is used as a secondary solvent to remove the hydrocarbon from extract phase.

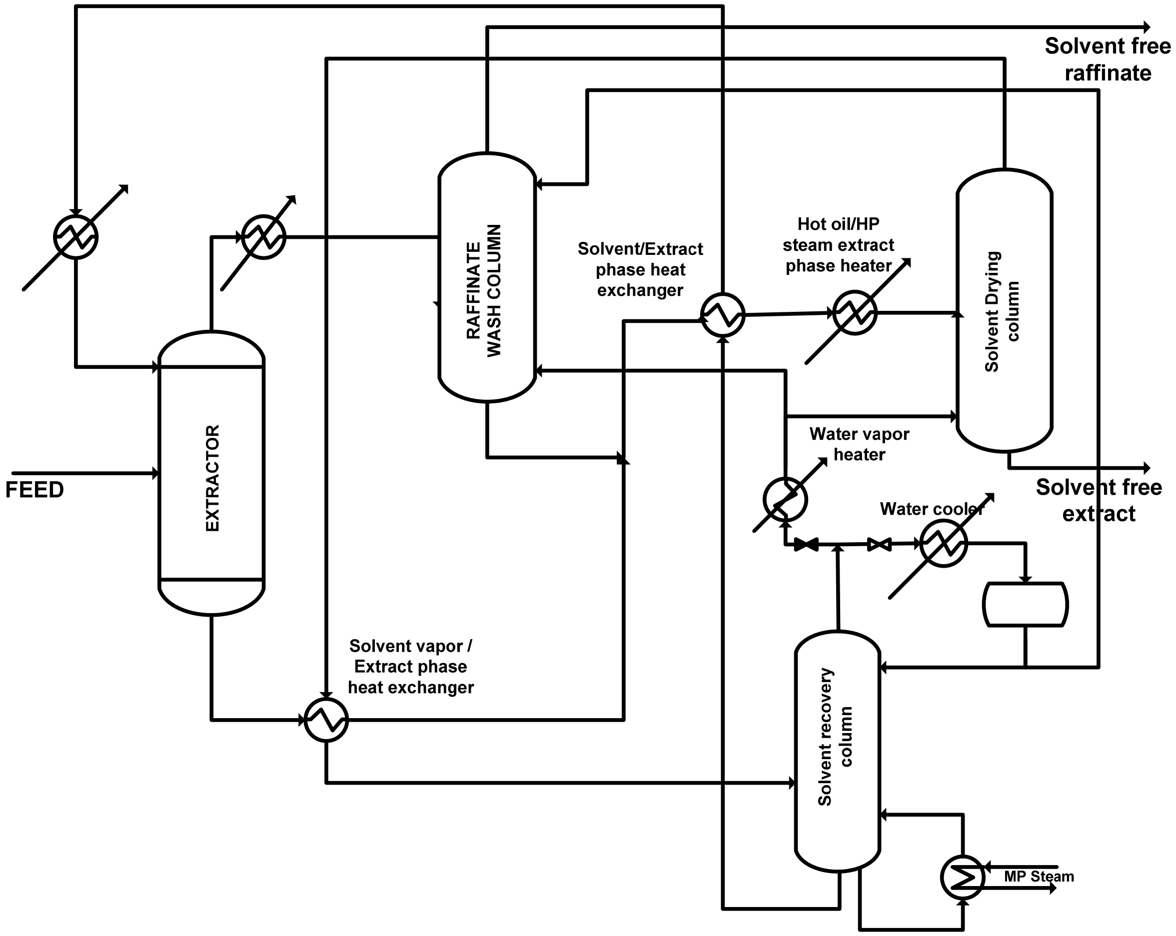


Figure 3.2. Process flow scheme of extraction and solvent recovery section for solvent vaporization route.

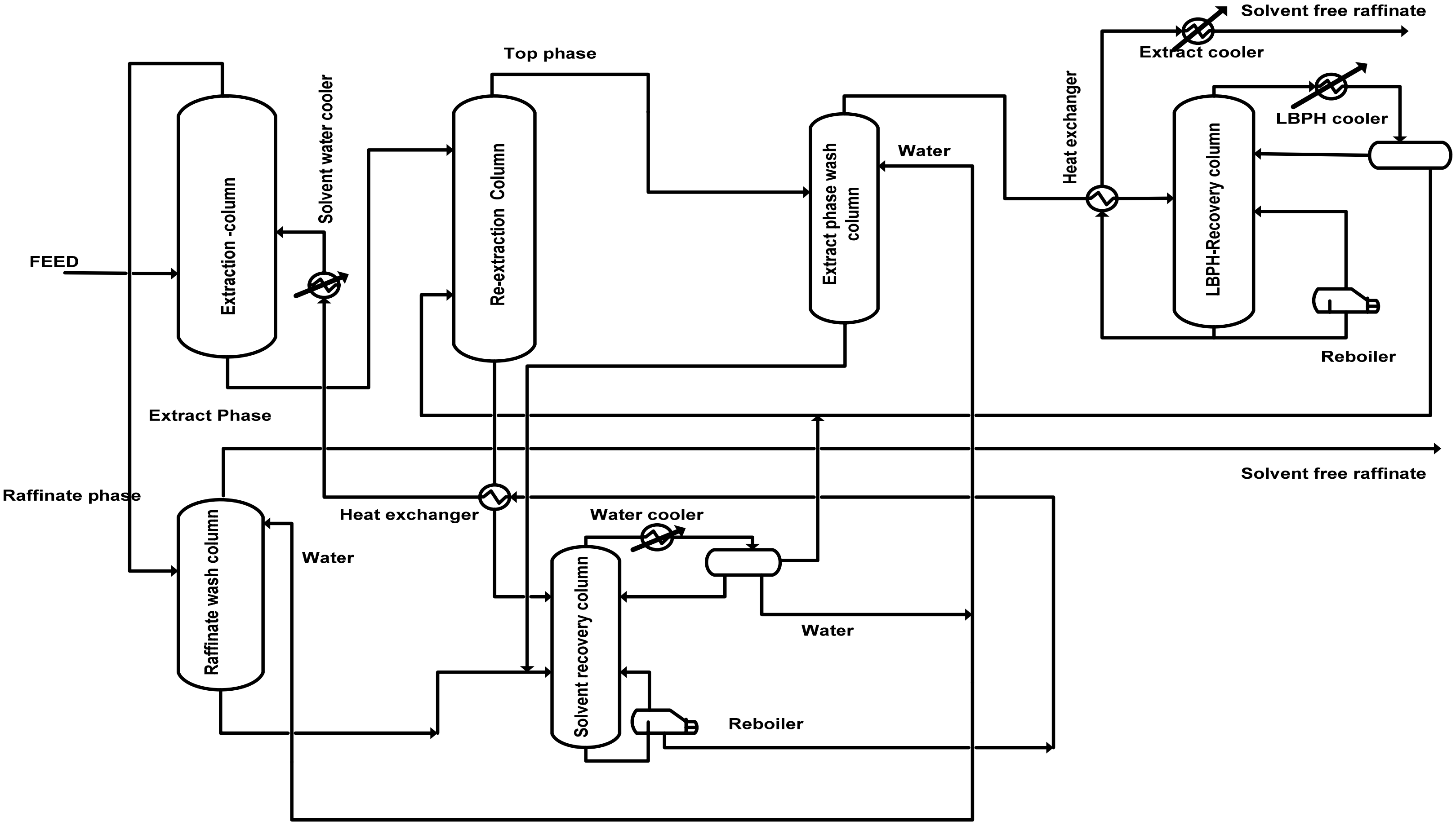


Figure 3.3. Process flow scheme of extraction and solvent recovery section for re-extraction route.

Hydrocarbon phase obtained from re-extraction column is water washed to remove the solvent. Solvent free extract phase is processed in distillation column to recover the LBH for its reuse. Solvent phase from re-extraction column and water from solvent washing columns are routed to solvent drying column to remove the excess water from the solvent. The solvent from drying column is re-circulated to the extraction column. At this point, it is essential to note that benzene, toluene and xylene (BTX) aromatics production from liquid-liquid extraction and extractive distillation processes using high boiling and very selective solvent like sulfolane is well established.

In aromatic extraction process, there is a need of very high purity of aromatics and pure solvent is recovered by vaporizing the aromatics from solvent. This is a reason that use of highly selective solvents having high boiling points are preferable as they provide very pure aromatics and lower reflux rate in solvent recovery column to avoid the solvent carry over with vaporized aromatics as a result lower energy requirement in solvent recovery. However, gas oil is a mixture of compounds and has boiling temperature range up to 370°C. This forces the complex design of solvent recovery section for high boiling point solvent (Figure 3.3) and suggests that best solvent having high boiling point for aromatic extraction may not be the best for gas oil desulfurization. Moreover, for solvent having boiling point less than gas oil, solvent will be vaporized and it is known that process energy required for vaporization is radically higher than sensible heating of a liquid. Thus, process energy consumption in solvent recovery section will depend on the solvent to feed ratio required in the process.

Solvent to feed ratio depends on the capacity and selectivity of solvent. P_I integrates the effect of these both parameters. Therefore, it is a reasonable assumption that process energy requirement has been integrated in performance factor of solvent for lower boiling solvents. It is acknowledged that requirement of more number of separation steps for the production of same products under similar operating conditions of temperature and pressure will increase the complexity of the process. Addition of a new column in process also includes the addition of auxiliary's equipments (pipelines, valves, pump, heater, etc.), their foundations and their operation. This will increase the required capital investment, operational and maintenance complexity. Process design for lower boiling point solvents to be recovered using vaporization route contains three columns for solvent recovery (Figure 3.2) whereas for high boiling point solvents to be recovered using re-extraction route contains five separation columns (Figure 3.3).

In view of above, it is clear that complexity of solvent recovery section in term of its operation and capital investment requirements should be integrated for getting realistic evaluation of having lower and higher boiling points. Hence, in present study, industrial usability indexes (S_{IUI}) of solvent was defined as a function of P_I, process complexity factor (P_{cf}) and uncertainty factor (U_f) to undertake the uncertainty in estimation of P_{cf} as:

$$S_{IUI} = P_I / (P_{cf} U_f) \tag{3.7}$$

The process complexity factor (P_{cf}) was estimated as the ratio of the number of separation columns required in re-extraction (Figure 3.3) and solvent vaporization (Figure 3.2) schemes.

3.3. ESTIMATION OF VAN DER WAALS VOLUME, MOLAR VOLUME AND SOLUBILITY PARAMETERS

These parameters for sulfur and nitrogen compounds were estimated using the commercial software, based on quantum mechanics, Materials Studio 7.0. The structure of compound was constructed in the visualizer using builder module of Materials Studio 7.0. Molecule was then geometrically optimized using the forcite module with COMPASS II force field. Smart algorithm was used with convergence tolerances of 0.001 kcal/mol for energy and 0.5 kcal/mol Å for force and maximum iterations was fixed at 500. The van der Waals volume of optimized molecular structure of compound was estimated using atom volumes and surfaces tool. Model system for each compound was constructed using amorphous cell module as an amorphous three-dimensional periodic box. 100 molecules in the cell constructed were selected so that the dimension of the cubic cell be sufficiently more than twice the cut-off distance (12.5 Å) for using the summation method (group based) for the electrostatic term. The initial density of bulk phase is required to build the proper model system. For solvents, nitrogen and certain hydrocarbons whose densities were available in published literature, the reported value was used as initial density input. For those sulfur compounds whose density is not available in recognized literature, the initial density value input was based on the value reported on www.chemspider.com and dynamic simulation using constant number of particles, pressure and temperature (NPT) ensembles was used to fine tune the density and to minimize the possibility of inaccuracy in reported value.

The cell constructed of known density compounds was then equilibrated using constant number of particles, volume and temperature (NVT) ensemble and then production run was carried out with the number of particles, volume and energy (NVE) ensemble using molecular dynamics. The cell constructed of sulfur compounds was equilibrated using NPT;

NVT ensembles followed by production run with NVE ensembles using molecular dynamics. The equilibrium and production runs were carried out for 100 ps with time step of 1 fs. Nosé-Hoover-Langevin (NHL) thermostats with Q ratio of 0.01 thermostat and Berendsen barostat were used in the simulation. Group based summation method with a chosen cut-off distance of 12.5 Å and spline width of 1 Å was used throughout the equilibration steps. The molar volume of compound was estimated using the predicted density of the system after NPT ensemble and molecular weight. The resulting molecular trajectories were then used in the cohesive energy density estimation using the forcite modules of martial studio software.

3.4. RESULTS AND DISCUSSION

3.4.1. Validation of Computation Method

It is essential to analyze the accuracy of the value of solubility parameters predicted from the simulation by comparing it with the experimental value reported in literature. In order to do this, paraffins, cycloparaffins, aromatics, nitrogen and sulfur compounds which have some structural similarity with gas oil compounds and potential solvents which can be used for desulfurization of gas oil were selected to test the accuracy of simulation method. The results of simulation are presented in Table 3.1. A good agreement (maximum percent deviation of 4%) between predicted and reported value of solubility parameters was found. This suggests that computational model is capable of predicting the solubility parameters of gas oil model components.

3.4.2. Molar volume (V_m), van der Waals volume (r_{vdw}), solubility parameters

Gas oil is a complex mixture of paraffins, cycloparaffins, aromatics, and sulfur and nitrogen compounds. n-tetradecane, 3-ethylbicyclo decane and propyl naphthalene were selected as model compounds to represent the paraffins, cycloparaffins and aromatics compounds of gas oil, respectively. BT, DBT and their derivatives were selected to represent the sulfur compounds. Nitrogen compounds were represented by quinoline, indole and carbazole. The molar volume (V_m) of n-tetradecane, 3-ethylbicyclo decane and propyl naphthalene and nitrogen compounds at 25°C were estimated using ASPEN HYSIS software.

Table 3.1. Solubility parameters at room temperature at 25°C.

Hydrocarbon type	Compound name	Solubility parameter $(J/cm^3)^{1/2}$ Literature	Predicted	Deviation (%)	Reference
Paraffin	Hexane	14.90	15.26	-2.4	Burke, 1984
Cycloparaffin	Methylcyclohexane	16.00	16.37	-2.3	Burke, 1984
Aromatic	Toluene	19.60	19.15	2.3	Belmares et al., 2004
	Napthalene	20.30	21.10	-3.9	Burke, 1984
Nitrogen	Pyridine	21.80	21.34	2.1	Derecskei and Kovacs, 2008
	Quinoline	22.00	22.28	-1.3	Burke, 1984
Sulfur	Carbon disulfide	20.50	20.47	0.1	Burke, 1984
Solvents	Dimethyl formamide	24.43	24.73	-1.2	Belmares et al., 2004
	Furfural	24.83	24.45	1.6	Hiroshi, 2010
	Dimethyl acetamide	22.08	22.96	-4.0	Belmares et al., 2004
	N methyl 2-pyrilidone	23.10	23.75	-2.8	Belmares et al., 2004

The r_{vdw} values for these compounds were estimated using the material studio 7.0. Solubility parameters of aromatics, and sulfur and nitrogen model compounds were also estimated using the material studio 7.0 as per procedure described in section 3.3. Solubility parameter of n-tetradecane was estimated using the heat of vaporization value reported in literature (API technical data book, 2006) as dynamic simulations failed for such a long chains compounds. The solubility parameter of conventional solvents was taken as an average of values reported in literature (Burke 1984; Charles, 2001; Belmares et al., 2004; http://www.accudynetest.com/solubility_table.html; Hiroshi, 2010; http://www.stenutz.eu/chem/solv6.php?name=N,N-dimethylacetamide; Dimethylacetamide technical data sheet; http://www.hansen-solubility.com/index.html; Tilstam, 2012) and values of V_m and r_{vdw} were estimated using the ASPEN HYSIS and material studio 7.0. Values of these parameters for IL solvents were taken from literature (Wang et al., 2013).

Values of above mentioned parameters for gas oil compounds are given in Table 3.2 and for solvents are in Table 3.3. Estimated values of standard heat of vaporization of gas oil model compounds using the solubility parameters are also given in Table 3.2.

Table 3.2. Molar volume (Vm), van der waals volume (r_{vdw}), solubility parameters (δ) and heat of vaporization of model gas oil compounds.

Model hydrocarbon name	**Nomenclature**	**V_m (cm^3/mol)**	**r_{vdw} (cm^3 /mol)**	**δ $(J/cm^3)^{1/2}$**	**Heat of vaporization (kJ/mol)**
N-tetradecane*	Ted-NP	260.6	159.2	15.61	67.37
3-Ethylbicycl decane	Ebcd-CP	188.50	115.3	18.30	65.59
1-n-propyl napthalene	Npn-A	222.20	107.0	19.44	86.44
Benzothiophene	BT	119.71	71.8	20.32	51.88
3-Methyl benzothiophene	MBT	138.66	81.7	19.86	57.14
3,5 Dimethyl benzothiophene	DMBT	156.16	91.8	19.43	61.40
2,3,4 trimethyl benzothiophene	TMBT	167.25	101.5	18.88	62.09
Di-benzothiophene	DBT	156.81	98.6	21.04	71.89
4-Methyl-DBT	MDBT	168.32	108.3	20.40	72.54
4,6 Dimethyl-DBT	DMDBT	185.10	118.1	19.97	76.27
Quinoline	Quin	118.60	74.0	21.80	58.83
Indole	Indo	106.50	67.6	24.26	65.15
Carbazole	Carba	139.00	103.6	20.38	60.23

Table 3.3. Molar volumes (V_m), van der waal volumes (r_{vdw}) and solubility parameters (δ) of solvents.

Full name	Nomencl-ature	Vm (cm^3/mol)	r_{vdW} (cm^3/mol)	δ (j/cm^3)
N,N dimethyl formamide	DMF	77.4	46.00	24.68(1)
Furfural	Furfural	85.4	51.4	24.47(2)
N,N dimethyl acetamide	DMA	93.1	56.2	22.42(3)
Dimethyl sulfoxide	DMSO	71.2	43.9	26.55(4)
N methyl pyrolidone	NMP	96.7	59.8	23.02(5)
Sulfolane	SULFO	95.7	61.6	27.20(6)
1-Methacryloyloxyhexyl-1-methylimidazolium Bromide	MIM1(7)	362.0	170.0	25.83
1-Propyl-2,3-dimethylimidazolium Tetrafluoroborate	MIM2(7)	168.0	197.0	23.99
1-Ethyl-3-methylimidazolium Tetrafluoroborate	MIM3(7)	159.0	177.0	24.41
1-Butyl-3-methylimidazolium Tetrafluoroborate	MIM4(7)	191.0	197.0	23.78
1-Hexyl-3-methylimidazolium Tetrafluoroborate	MIM5(7)	225.0	218.0	22.76
1-Octyl-3-methylimidazolium Tetrafluoroborate	MIM6(7)	264.0	238.0	22.00
1-Hexadecyl-3-methylimidazolium Tetrafluoroborate	MIM7(7)	577.0	320.0	20.23
1-(2-Hydroxyethyl)-3-methylimidazolium Tetrafluoroborate	MIM8(7)	144.0	192.0	24.76
1-Butyl-3-methylimidazolium Hexafluorophosphate	MIM9(7)	211.0	143.0	22.06
1-Hexyl-3-methylimidazolium Hexafluorophosphate	MIM10(7)	245.0	163.0	22.18
1-Octyl-3-methylimidazolium Hexafluorophosphate	MIM11(7)	279.0	184.0	21.19
1-Methyl-3-methylimidazolium	MIM12(7)	244.0	154.0	24.71

Full name	**Nomencl-ature**	**Vm (cm^3/mol)**	**r_{vdW} (cm^3/mol)**	**δ (j/cm^3)**
Bis(trifluoromethylsulfonyl)imide				
1-Ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide	MIM13(7)	262.0	165.0	22.40
1-Butyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide	MIM14(7)	297.0	186.0	23.46
1-Methyl-3-methylimidazolium Dimethylphosphate	MIM15(7)	179.0	120.0	25.08
1-Ethyl-3-methylimidazolium Ethylsulfate	MIM16(7)	236.0	127.0	24.26
1-Methyl-3-methylimidazolium Methoxyethylsulfate	MIM17(7)	195.0	140.0	25.03
1-Butyl-3-methylimidazolium Trifluoromethanesulfonate	MIM18(7)	222.0	143.0	25.85
1-Butyl-3-methylimidazolium Diethyleneglycolmonomethylethersulfate	MIM19(7)	284.0	194.0	24.80
1-Hexyloxymethyl-3-methyl-imidazolium Bis(trifluoromethylsulfonyl)imide	MIM20(7)	350.0	219.0	21.04
1,3-Dihexyloxymethylimidazolium Bis(trifluoromethylsulfonyl)imide	MIM21(7)	460.0	284.0	20.59
1-Butyl-3-methylimidazolium Octylsulfate	MIM22(7)	328.0	218.0	22.83

(1) to (7) represents the average value of δ reported in references:

(1): Burke 1984, Belmares et al., 2004, and http://www.accudynetest.com/solubility_table.html

(2): Charles, 2001 and Hiroshi, 2010

(3): Belmares et al., 2004, http://www.stenutz.eu/chem/solv6.php?name=N,N-dimethylacetamide and Dimethylacetamide technical data sheet.

(4): Burke 1984 and Web. < http://www.accudynetest.com/solubility_table.html >

(5): Belmares et al., 2004, http://www.hansen-solubility.com/index.html and Tilstam, 2012

(6): Derecskei and Kovacs, 2008

(7): Wang et al., 2013

It is important to note that there is scarcity of the solubility parameters of model compounds representing the gas oil in literature. The V_m, r_{vdw}, and solubility parameters (Table 3.2) of these compounds can be used for the estimation of activity coefficients. The capacity and selectivity of solvents for given compounds can be estimated using their activity coefficients. Activity coefficients can also be used to regress the interaction parameter of these compounds with the different solvents. These interaction parameters are essential in commercial simulator for simulating the gas oil solvent extraction process to analyze the separation of sulfur and nitrogen compounds and solvent recovery section for its recovery from extract and raffinate phase.

3.4.3. Capacity and Selectivity of Solvents

Capacity and selectivity are important properties of solvent and can be used as a parameter for their selection in extraction process. Capacity and selectivity of selected solvents were estimated using equations 3.3-3.5. The estimated values of capacity of solvents for model compounds are given Table 3.4. The solubility of model compounds in solvents followed the trend n-paraffins < cycloparaffins < aromatic < sulfur compound < nitrogen compounds. It is clear that solubility of undesired compounds (sulfur, nitrogen and polyaromatics) is significantly higher than the desired compounds. It suggests that refractive sulfur and nitrogen compounds which reduce the desulfurization performance of hydrotreater can be removed using solvent extraction.

In solvent extraction process, it is desirable to minimize the loss of desired compounds with the extract phase. The selectivity of solvent for undesired compound with respect to desired compounds is used to analyze this effect. High value of selectivity of solvent for solute provides better separation between the solute and carrier compounds. In present study, selectivity of solvents for sulfur and nitrogen compounds with respect to n-paraffin, cycloparaffin and aromatic were estimated and are given in Tables 3.5-3.7, respectively. Selectivity values of solvent for sulfur and nitrogen compounds w.r.t. paraffins were found drastically higher in comparison to cycloparaffins and aromatic, whereas, w.r.t. cycloparaffins and aromatic are comparable. It is important to note that n-paraffins and cycloparaffins are most desirable compounds in gas oil. Considering this, the selectivity of sulfur and nitrogen compounds with respect to cycloparaffins was selected for rating of the solvents.

Table 3.4: Capacity of model compounds in solvents.

Solvent	BT	MBT	DMBT	TMBT	DBT	DBT	DM DBT	Quin	Indo	Carba	Ted-NP	Ebcd-CP	Npn-A
DMF	0.418	0.295	0.199	0.122	0.504	0.352	0.243	0.710	1.029	0.424	0.000	0.057	0.103
Furfural	0.446	0.320	0.219	0.137	0.530	0.376	0.265	0.734	1.016	0.446	0.000	0.066	0.119
DMA	0.819	0.716	0.603	0.469	0.960	0.847	0.738	0.999	0.872	0.872	0.010	0.314	0.502
DMSO	0.162	0.090	0.047	0.023	0.174	0.096	0.052	0.363	0.835	0.145	0.000	0.007	0.013
NMP	0.708	0.584	0.463	0.337	0.830	0.687	0.562	0.941	0.939	0.731	0.004	0.205	0.345
SULFO	0.102	0.050	0.023	0.010	0.096	0.047	0.022	0.249	0.691	0.079	0.000	0.003	0.005
MIM1	0.264	0.150	0.081	0.040	0.248	0.141	0.079	0.522	1.051	0.199	0.000	0.014	0.027
MIM2	0.625	0.443	0.300	0.187	0.632	0.447	0.314	0.945	1.222	0.522	0.001	0.090	0.168
MIM3	0.516	0.351	0.227	0.135	0.521	0.352	0.237	0.830	1.182	0.426	0.000	0.061	0.115
MIM4	0.672	0.487	0.338	0.215	0.681	0.494	0.356	0.986	1.213	0.567	0.001	0.108	0.198
MIM5	0.931	0.743	0.570	0.404	0.933	0.753	0.601	1.177	1.153	0.809	0.005	0.238	0.410
MIM6	1.118	0.947	0.776	0.593	1.089	0.945	0.807	1.266	1.053	0.983	0.014	0.390	0.626
MIM7	1.441	1.357	1.254	1.113	1.221	1.229	1.190	1.265	0.736	1.249	0.116	0.907	1.169
MIM8	0.458	0.298	0.184	0.105	0.454	0.294	0.188	0.775	1.202	0.368	0.000	0.044	0.084
MIM9	0.945	0.811	0.672	0.517	0.963	0.843	0.727	1.084	0.903	0.873	0.013	0.344	0.550
MIM10	0.958	0.810	0.661	0.501	0.969	0.835	0.709	1.117	0.958	0.870	0.011	0.326	0.528
MIM11	1.132	1.024	0.901	0.747	1.077	1.014	0.931	1.144	0.799	1.029	0.038	0.553	0.805
MIM12	0.439	0.289	0.181	0.104	0.444	0.291	0.189	0.738	1.125	0.361	0.000	0.045	0.085
MIM13	0.922	0.765	0.612	0.454	0.938	0.790	0.658	1.109	0.998	0.832	0.008	0.285	0.473
MIM14	0.731	0.549	0.394	0.261	0.746	0.561	0.419	1.024	1.170	0.629	0.002	0.138	0.249
MIM15	0.352	0.224	0.135	0.075	0.359	0.227	0.142	0.626	1.036	0.292	0.000	0.030	0.058
MIM16	0.503	0.351	0.234	0.143	0.526	0.366	0.253	0.793	1.080	0.434	0.000	0.067	0.125
MIM17	0.372	0.237	0.143	0.079	0.374	0.237	0.148	0.656	1.078	0.304	0.000	0.032	0.062
MIM18	0.249	0.142	0.077	0.039	0.238	0.135	0.076	0.496	0.998	0.191	0.000	0.013	0.026
MIM19	0.452	0.292	0.180	0.102	0.446	0.287	0.183	0.769	1.204	0.361	0.000	0.042	0.081
MIM20	1.214	1.102	0.975	0.816	1.127	1.070	0.988	1.199	0.815	1.086	0.046	0.611	0.876
MIM21	1.367	1.267	1.148	0.992	1.205	1.181	1.120	1.265	0.789	1.198	0.078	0.778	1.055
MIM22	0.916	0.726	0.553	0.389	0.919	0.736	0.583	1.169	1.163	0.794	0.004	0.227	0.393

Table 3.5. Selectivity of solvents for sulfur compounds and nitrogen compounds with respect to n-tetradecane.

Solvent	BT	MBT	DMBT	TMBT	DBT	MDBT	DM DBT	Quin	Indo	Carba
DMF	1520	1074	722	443	1832	1278	884	2582	3739	1540
Furfural	1192	856	585	365	1416	1005	708	1961	2715	1191
DMA	79	69	58	45	93	82	72	97	84	85
DMSO	27567	15336	8066	3917	29700	16401	8872	61413	140160	24641
NMP	175	145	115	83	205	170	139	233	232	181
SULFO	109169	53426	24694	10655	102556	50328	24012	267412	741099	84687
MIM1	15663	8919	4813	2398	14724	8353	4677	31004	62354	11803
MIM2	1004	712	482	300	1015	718	505	1518	1962	839
MIM3	1785	1212	784	466	1801	1218	818	2870	4085	1474
MIM4	749	543	376	240	759	550	396	1098	1352	632
MIM5	198	158	121	86	199	160	128	251	245	172
MIM6	80	67	55	42	78	67	57	90	75	70
MIM7	12	12	11	10	11	11	10	11	6	11
MIM8	3054	1985	1228	698	3021	1955	1255	5163	8004	2450
MIM9	75	65	53	41	77	67	58	86	72	69
MIM10	90	76	62	47	91	78	67	105	90	82
MIM11	30	27	24	20	28	27	25	30	21	27
MIM12	2675	1763	1105	636	2704	1772	1152	4498	6856	2202
MIM13	118	98	78	58	120	101	84	142	128	107
MIM14	477	358	257	170	487	366	273	668	763	410
MIM15	4336	2758	1667	925	4422	2793	1748	7713	12773	3593
MIM16	1306	913	609	372	1367	951	657	2060	2808	1129
MIM17	4217	2682	1621	900	4241	2681	1680	7436	12216	3439
MIM18	15417	8810	4770	2383	14708	8368	4697	30650	61699	11823
MIM19	3250	2102	1294	731	3208	2065	1319	5528	8654	2599
MIM20	26	24	21	18	25	23	22	26	18	24
MIM21	17	16	15	13	15	15	14	16	10	15
MIM22	217	172	131	92	217	174	138	277	275	188

Table 3.6. Selectivity of solvents for sulfur compounds and nitrogen compounds with respect to 3-ethylbicycl decane.

Solvent	BT	MBT	DMBT	TMBT	DBT	MDBT	DM DBT	Quin	Indo	Carba
DMF	7.35	5.19	3.49	2.14	8.86	6.18	4.28	12.49	18.08	7.45
Furfural	6.79	4.88	3.34	2.08	8.07	5.73	4.03	11.17	15.47	6.79
DMA	2.60	2.28	1.92	1.49	3.05	2.70	2.35	3.18	2.77	2.77
DMSO	21.83	12.14	6.39	3.10	23.52	12.99	7.03	48.63	110.99	19.51
NMP	3.45	2.85	2.26	1.64	4.05	3.35	2.74	4.59	4.58	3.56
SULFO	38.22	18.71	8.65	3.73	35.91	17.62	8.41	93.63	259.48	29.65
MIM1	19.17	10.92	5.89	2.94	18.02	10.22	5.72	37.95	76.32	14.45
MIM2	6.95	4.93	3.34	2.07	7.02	4.97	3.49	10.50	13.58	5.80
MIM3	8.54	5.80	3.75	2.23	8.61	5.82	3.91	13.72	19.53	7.05
MIM4	6.25	4.53	3.14	2.00	6.34	4.59	3.31	9.16	11.28	5.27
MIM5	3.91	3.12	2.39	1.70	3.92	3.16	2.53	4.95	4.85	3.40
MIM6	2.87	2.43	1.99	1.52	2.79	2.43	2.07	3.25	2.70	2.52
MIM7	1.59	1.50	1.38	1.23	1.35	1.35	1.31	1.39	0.81	1.38
MIM8	10.44	6.79	4.20	2.39	10.33	6.68	4.29	17.65	27.36	8.37
MIM9	2.75	2.36	1.95	1.50	2.80	2.45	2.11	3.15	2.63	2.54
MIM10	2.94	2.49	2.03	1.54	2.97	2.56	2.18	3.43	2.94	2.67
MIM11	2.05	1.85	1.63	1.35	1.95	1.83	1.68	2.07	1.45	1.86
MIM12	9.85	6.49	4.07	2.34	9.95	6.52	4.24	16.56	25.24	8.11
MIM13	3.23	2.68	2.15	1.59	3.29	2.77	2.30	3.88	3.50	2.91
MIM14	5.30	3.98	2.86	1.89	5.41	4.07	3.04	7.42	8.48	4.56
MIM15	11.64	7.40	4.47	2.48	11.87	7.50	4.69	20.70	34.29	9.65
MIM16	7.50	5.24	3.49	2.13	7.84	5.46	3.77	11.82	16.11	6.48
MIM17	11.61	7.38	4.46	2.48	11.67	7.38	4.62	20.47	33.63	9.47
MIM18	18.92	10.81	5.85	2.92	18.05	10.27	5.76	37.61	75.71	14.51
MIM19	10.69	6.91	4.25	2.40	10.55	6.79	4.34	18.17	28.45	8.54
MIM20	1.99	1.80	1.60	1.33	1.84	1.75	1.62	1.96	1.33	1.78
MIM21	1.76	1.63	1.47	1.27	1.55	1.52	1.44	1.62	1.01	1.54
MIM22	4.04	3.20	2.44	1.72	4.05	3.25	2.57	5.16	5.13	3.50

Table 3.7. Selectivity of solvents for sulfur compounds and nitrogen compounds with respect to 1-n-propyl napthalene.

Solvent	BT	MBT	DMBT	TMBT	DBT	MDBT	DM DBT	Quin	Indo	Carba
DMF	7.35	5.19	3.49	2.14	8.86	6.18	4.28	12.49	18.08	7.45
Furfural	6.79	4.88	3.34	2.08	8.07	5.73	4.03	11.17	15.47	6.79
DMA	2.60	2.28	1.92	1.49	3.05	2.70	2.35	3.18	2.77	2.77
DMSO	21.83	12.14	6.39	3.10	23.52	12.99	7.03	48.63	110.99	19.51
NMP	3.45	2.85	2.26	1.64	4.05	3.35	2.74	4.59	4.58	3.56
SULFO	38.22	18.71	8.65	3.73	35.91	17.62	8.41	93.63	259.48	29.65
MIM1	19.17	10.92	5.89	2.94	18.02	10.22	5.72	37.95	76.32	14.45
MIM2	6.95	4.93	3.34	2.07	7.02	4.97	3.49	10.50	13.58	5.80
MIM3	8.54	5.80	3.75	2.23	8.61	5.82	3.91	13.72	19.53	7.05
MIM4	6.25	4.53	3.14	2.00	6.34	4.59	3.31	9.16	11.28	5.27
MIM5	3.91	3.12	2.39	1.70	3.92	3.16	2.53	4.95	4.85	3.40
MIM6	2.87	2.43	1.99	1.52	2.79	2.43	2.07	3.25	2.70	2.52
MIM7	1.59	1.50	1.38	1.23	1.35	1.35	1.31	1.39	0.81	1.38
MIM8	10.44	6.79	4.20	2.39	10.33	6.68	4.29	17.65	27.36	8.37
MIM9	2.75	2.36	1.95	1.50	2.80	2.45	2.11	3.15	2.63	2.54
MIM10	2.94	2.49	2.03	1.54	2.97	2.56	2.18	3.43	2.94	2.67
MIM11	2.05	1.85	1.63	1.35	1.95	1.83	1.68	2.07	1.45	1.86
MIM12	9.85	6.49	4.07	2.34	9.95	6.52	4.24	16.56	25.24	8.11
MIM13	3.23	2.68	2.15	1.59	3.29	2.77	2.30	3.88	3.50	2.91
MIM14	5.30	3.98	2.86	1.89	5.41	4.07	3.04	7.42	8.48	4.56
MIM15	11.64	7.40	4.47	2.48	11.87	7.50	4.69	20.70	34.29	9.65
MIM16	7.50	5.24	3.49	2.13	7.84	5.46	3.77	11.82	16.11	6.48
MIM17	11.61	7.38	4.46	2.48	11.67	7.38	4.62	20.47	33.63	9.47
MIM18	18.92	10.81	5.85	2.92	18.05	10.27	5.76	37.61	75.71	14.51
MIM19	10.69	6.91	4.25	2.40	10.55	6.79	4.34	18.17	28.45	8.54
MIM20	1.99	1.80	1.60	1.33	1.84	1.75	1.62	1.96	1.33	1.78
MIM21	1.76	1.63	1.47	1.27	1.55	1.52	1.44	1.62	1.01	1.54
MIM22	4.04	3.20	2.44	1.72	4.05	3.25	2.57	5.16	5.13	3.50

It is seen that selectivity of DMF, furfural, DMA, DMSO and NMP solvents for sulfur compounds follows the order: DBT > BT > 4MDBT > 3MBT > 4,6 DMDBT > 3,5DMBT > 2,3,6 DMDBT whereas sulfolane and imidazolium based IL solvents follow the order: BT > DBT > 3MBT > 4MDBT > 4,6 DMDBT > 3,5 DMBT > 2,3,6 TMDBT. The solvents having high capacity for nitrogen compounds followed the selectivity order: indole > quinoline > carbazole whereas for higher selective solvents the order is: quinoline > indole > carbazole. It is observed that selectivity and capacity values of solvents for nitrogen compounds are higher than most of the sulfur compounds. This suggests that nitrogen compounds are easier to remove than sulfur compounds and will remove simultaneously.

The ranking of solvent based on their capacity shown in Table 3.8 reveals that top 5 solvents for all sulfur and nitrogen compounds are all ILs. It is observed that position of solvents other than top 5 changes with respect to the type of sulfur compounds. However, for nitrogen compounds, position of all the solvent changes with respect to the type of nitrogen compounds which suggests that one solvent can be the best for either quinoline or indole or carbazole removal and not for removal of all nitrogen compounds.

Anantharaj and Banerjee (2011a) reported the capacity and selectivity trend of 1-Ethyl-3-methylimidazolium Tetrafluoroborate (MIM3); 1-Ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide (MIM13) and 1-Ethyl-3-methylimidazolium Ethylsulfate (MIM16) ILs for removal of benzothiophene and DBT sulfur compounds. In these studies, capacity ranking of these solvents for benzothiophene and DBT was in the same order: MIM13 > MIM3 ≈ MIM16. In the present study, capacity ranking of these solvents for benzothiophene also followed the same order MIM13 > MIM3 ≈ MIM16 and for DBT MIM13 > MIM16 ≈ MIM3. Anantharaj and Banerjee (2011a) reported the selectivity ranking of these solvents for benzothiophene in order: MIM3 > MIM3 ≈ MIM16 and for DBT in the order: MIM13 ≈ MIM3 > MIM16. In the present study, the selectivity ranking of these solvents for benzothiophene and DBT followed the order MIM3 ≈ MIM16 > MIM13. However, the ranking order in the present study seem realistic in view of the fact that for solvents having different capacities, selectivity generally follows the reverse order of capacity.

The analysis of top 5 solvents in Table 3.9 indicates that solvents such as sulfolane, DMSO, MIM1, MIM18 and MIM15 which are of lower capacity show higher selectivity. This clearly suggests that there is reverse trend between capacity and selectivity of solvents. Hence, selection of solvents cannot be done either based on capacity or selectivity.

Table 3.8. Ranking of solvents based on their capacity index.

BT	MBT	DMBT	TMBT	DBT	MDBT	DM DBT	Quin	Indo	Carba
MIM7	MIM7	MIM7	MIM7	MIM7	MIM7	MIM7	MIM6	MIM2	MIM7
MIM21	MIM21	MIM21	MIM21	MIM21	MIM21	MIM21	MIM7	MIM4	MIM21
MIM20	MIM20	MIM20	MIM20	MIM20	MIM20	MIM20	MIM21	MIM19	MIM20
MIM11	MIM11	MIM11	MIM11	MIM6	MIM11	MIM11	MIM20	MIM8	MIM11
MIM6	MIM6	MIM6	MIM6	MIM11	MIM6	MIM6	MIM5	MIM3	MIM6
MIM10	MIM9	MIM9	MIM9	MIM10	DMA	DMA	MIM22	MIM14	MIM9
MIM9	MIM10	MIM10	MIM10	MIM9	MIM9	MIM9	MIM11	MIM22	DMA
MIM5	MIM13	MIM13	DMA	DMA	MIM10	MIM10	MIM10	MIM5	MIM10
MIM13	MIM5	DMA	MIM13	MIM13	MIM13	MIM13	MIM13	MIM12	MIM13
MIM22	MIM22	MIM5	MIM5	MIM5	MIM5	MIM5	MIM9	MIM16	MIM5
DMA	DMA	MIM22	MIM22	MIM22	MIM22	MIM22	MIM14	MIM17	MIM22
MIM14	NMP	NMP	NMP	NMP	NMP	NMP	DMA	MIM6	NMP
NMP	MIM14	MIM14	MIM14	MIM14	MIM14	MIM14	MIM4	MIM1	MIM14
MIM4	MIM4	MIM4	MIM4	MIM4	MIM4	MIM4	MIM2	MIM15	MIM4
MIM2	MIM2	MIM2	MIM2	MIM2	MIM2	MIM2	NMP	DMF	MIM2
MIM3	MIM16	MIM16	MIM16	Furfu	Furfu	Furfu	MIM3	Furfu	Furfu
MIM16	MIM3	MIM3	Furfu	MIM16	MIM16	MIM16	MIM16	MIM13	MIM16
MIM8	Furfu	Furfu	MIM3	MIM3	MIM3	DMF	MIM8	MIM18	MIM3
MIM19	MIM8	DMF	DMF	DMF	DMF	MIM3	MIM19	MIM10	DMF
Furfu	DMF	MIM8	MIM8	MIM8	MIM8	MIM12	MIM12	NMP	MIM8
MIM12	MIM19	MIM12	MIM12	MIM19	MIM12	MIM8	Furfural	MIM9	MIM19
DMF	MIM12	MIM19	MIM19	MIM12	MIM19	MIM19	DMF	DMA	MIM12
MIM17	MIM17	MIM17	MIM17	MIM17	MIM17	MIM17	MIM17	DMSO	MIM17
MIM15	MIM15	MIM15	MIM15	MIM15	MIM15	MIM15	MIM15	MIM20	MIM15
MIM1	MIM1	MIM1	MIM1	MIM1	MIM1	MIM1	MIM1	MIM11	MIM1
MIM18	MIM18	MIM18	MIM18	MIM18	MIM18	MIM18	MIM18	MIM21	MIM18
DMSO	DMSO	DMSO	DMSO	DMSO	DMSO	DMSO	DMSO	MIM7	DMSO
SULFO	SULFO	SULFO	SULFO	SULFO	SULFO	SULFO	SULFO	SULFO	SULFO

Table 3.9. Ranking of solvents based on their selectivity for sulfur compounds and nitrogen compounds with respect to 3-ethylbicycl decane.

BT	**MBT**	**DMBT**	**TMBT**	**DBT**	**MDBT**	**DM DBT**	**Quin**	**Indo**	**Carba**
SULFO	SULFO	SULFO	SULFO	SULFO	SULFO	SULFO	SULFO	SULFO	SULFO
DMSO	DMSO	DMSO	DMSO	DMSO	DMSO	DMSO	DMSO	DMSO	DMSO
MIM1	MIM1	MIM1	MIM1	MIM18	MIM18	MIM18	MIM1	MIM1	MIM18
MIM18	MIM18	MIM18	MIM18	MIM1	MIM1	MIM1	MIM18	MIM18	MIM1
MIM15	MIM15	MIM15	MIM15	MIM15	MIM15	MIM15	MIM15	MIM15	MIM15
MIM17	MIM17	MIM17	MIM17	MIM17	MIM17	MIM17	MIM17	MIM17	MIM17
MIM19	MIM19	MIM19	MIM19	MIM19	MIM19	MIM19	MIM19	MIM19	MIM19
MIM8	MIM8	MIM8	MIM8	MIM8	MIM8	MIM8	MIM8	MIM8	MIM8
MIM12	MIM12	MIM12	MIM12	MIM12	MIM12	DMF	MIM12	MIM12	MIM12
MIM3	MIM3	MIM3	MIM3	DMF	DMF	MIM12	MIM3	MIM3	DMF
MIM16	MIM16	MIM16	DMF	MIM3	MIM3	Furfu	DMF	DMF	MIM3
DMF	DMF	DMF	MIM16	Furfu	Furfu	MIM3	MIM16	MIM16	Furfu
MIM2	MIM2	MIM2	Furfu	MIM16	MIM16	MIM16	Furfu	Furful	MIM16
Furfu	Furfu	Furfu	MIM2	MIM2	MIM2	MIM2	MIM2	MIM2	MIM2
MIM4	MIM4	MIM4	MIM4	MIM4	MIM4	MIM4	MIM4	MIM4	MIM4
MIM14	MIM14	MIM14	MIM14	MIM14	MIM14	MIM14	MIM14	MIM14	MIM14
MIM22	MIM22	MIM22	MIM22	MIM22	NMP	NMP	MIM22	MIM22	NMP
MIM5	MIM5	MIM5	MIM5	NMP	MIM22	MIM22	MIM5	MIM5	MIM22
NMP	NMP	NMP	NMP	MIM5	MIM5	MIM5	NMP	NMP	MIM5
MIM13	MIM13	MIM13	MIM13	MIM13	MIM13	DMA	MIM13	MIM13	MIM13
MIM10	MIM10	MIM10	MIM10	DMA	DMA	MIM13	MIM10	MIM10	DMA
MIM6	MIM6	MIM6	MIM6	MIM10	MIM10	MIM10	MIM6	DMA	MIM10
MIM9	MIM9	MIM9	MIM9	MIM9	MIM9	MIM9	DMA	MIM6	MIM9
DMA	DMA	DMA	DMA	MIM6	MIM6	MIM6	MIM9	MIM9	MIM6
MIM11	MIM11	MIM11	MIM11	MIM11	MIM11	MIM11	MIM11	MIM11	MIM11
MIM20	MIM20	MIM20	MIM20	MIM20	MIM20	MIM20	MIM20	MIM20	MIM20
MIM21	MIM21	MIM21	MIM21	MIM21	MIM21	MIM21	MIM21	MIM21	MIM21
MIM7	MIM7	MIM7	MIM7	MIM7	MIM7	MIM7	MIM7	MIM7	MIM7

3.4.4. Performance index (P_I) and Industrial Usability Index (S_{IUI}) of Solvents

P_I values of solvents were estimated for all model sulfur and nitrogen compounds using the equation 3.5 and are given in Table 3.10. Solvents ranking based on their P_I values for sulfur and nitrogen compounds is given in Table 3.11. This reveals that MIM1 for BT, MIM22 for MBT and MDBT, MIM7 for DMBT and TMBT, MIM 19 for DBT, DMA for DMDBT, sulfolane for indole and quinoline, DMF for carbazole are the best solvent on P_I scale. It is important to note that all top 5 solvents for benzothiophenic sulfur compounds are ILs. Whereas for removal of dibenzothiophenic sulfur compounds, conventional solvents also are among the top 5 solvents and their ranking are: DMF 5th for DBT; NMP 3rd for MDBT; and DMA 1st for DMDBT. For nitrogen compounds, ranking of conventional solvents are: sulfolane 1st and DMSO 4th for quinoline; sulfolane 1st and DMSO 2nd for indole; DMF 1st and furfural 5th for carbazole. Ranking of solvents based on P_I implies that solvents showing highest capacity or selectivity may not be best solvent for different sulfur and nitrogen compounds removal. It is also clear that there is no single solvent which performs best for removal of all sulfur and nitrogen compounds; and solvent selection can only be done based on detailed sulfur and nitrogen compounds analysis of gas oil.

In view of solvents' industrial application, S_{IUI} of solvents was estimated using equation 3.6. The process complexity factor (P_{cf}) of 1.0 was used for solvents having boiling point less than gas oil and can be recovered using the solvent recovery section shown in Figure 3.2. However, for solvents having boiling point more than gas oil, P_{cf} value of 1.67 was used. The estimated values of S_{IUI} for P_{cf} value of 1.67 and U_f value of 1.0 are given in Table 3.12. S_{IUI} based ranking of solvents is shown in Table 3.13. It can be seen clearly that dominance of conventional solvents increases in the top 5 solvents against the predominant dominance of IL solvents on P_I index scale. This implies that complexity in solvent recovery is very important aspect to be included in solvent screening and evaluation.

Further, it is understood that there are chances of uncertainty in P_{cf} estimations which need detail and rigorous simulations and costing of the solvent recovery section. Rigorous simulations and exact costing can be done only after extensive experimental and engineering work. Considering the approximation of ±20%, S_{IUI} were also estimated with ±20% value of uncertainty factor (U_f). The ranking of solvents for U_f=0.8 and U_f=1.2 are given in Table 3.14 and 3.15, respectively.

Table 3.10. Performance index of solvents for sulfur compounds and nitrogen compounds using selectivity with respect to 3-ethylbicycl decane.

Solvent	BT	MBT	DMBT	TMBT	DBT	MDBT	DM DBT	Quin	Indo	Carba
DMF	3.07	1.53	0.69	0.26	4.46	2.17	1.04	8.87	18.60	3.15
Furfural	3.03	1.56	0.73	0.28	4.27	2.15	1.07	8.20	15.72	3.02
DMA	2.13	1.63	1.16	0.70	2.93	2.28	1.73	3.18	2.42	2.42
DMSO	3.61	1.12	0.31	0.07	4.19	1.28	0.37	17.90	93.25	2.88
NMP	2.44	1.67	1.05	0.55	3.36	2.30	1.54	4.32	4.30	2.61
SULFO	3.89	0.93	0.20	0.04	3.43	0.83	0.19	23.34	179.25	2.34
MIM1	5.06	1.64	0.48	0.12	4.47	1.44	0.45	19.83	80.19	2.87
MIM2	4.35	2.18	1.00	0.39	4.44	2.22	1.10	9.93	16.58	3.03
MIM3	4.41	2.03	0.85	0.30	4.49	2.05	0.93	11.39	23.09	3.00
MIM4	4.20	2.21	1.06	0.43	4.32	2.27	1.18	9.03	13.69	2.99
MIM5	3.64	2.32	1.36	0.69	3.66	2.38	1.52	5.82	5.59	2.75
MIM6	3.21	2.30	1.55	0.90	3.04	2.29	1.67	4.12	2.85	2.48
MIM7	2.29	2.03	1.73	1.37	1.64	1.66	1.56	1.76	0.60	1.72
MIM8	4.79	2.02	0.77	0.25	4.68	1.96	0.81	13.68	32.88	3.08
MIM9	2.60	1.91	1.31	0.78	2.70	2.07	1.53	3.41	2.37	2.21
MIM10	2.82	2.01	1.34	0.77	2.88	2.14	1.54	3.83	2.82	2.32
MIM11	2.32	1.90	1.47	1.01	2.10	1.86	1.57	2.37	1.15	1.91
MIM12	4.32	1.88	0.74	0.24	4.42	1.90	0.80	12.22	28.39	2.93
MIM13	2.98	2.05	1.31	0.72	3.08	2.19	1.52	4.31	3.49	2.42
MIM14	3.88	2.18	1.13	0.49	4.04	2.29	1.27	7.60	9.92	2.87
MIM15	4.10	1.66	0.61	0.19	4.26	1.70	0.67	12.96	35.54	2.81
MIM16	3.77	1.84	0.82	0.31	4.12	2.00	0.95	9.37	17.41	2.81
MIM17	4.32	1.75	0.64	0.20	4.37	1.75	0.69	13.43	36.26	2.87
MIM18	4.72	1.54	0.45	0.11	4.29	1.39	0.44	18.64	75.53	2.77
MIM19	4.83	2.02	0.77	0.24	4.71	1.95	0.80	13.97	34.25	3.09
MIM20	2.41	1.99	1.56	1.09	2.08	1.87	1.60	2.35	1.09	1.93
MIM21	2.40	2.06	1.69	1.26	1.87	1.79	1.61	2.05	0.80	1.84
MIM22	3.70	2.32	1.35	0.67	3.72	2.39	1.50	6.03	5.97	2.78

Table 3.11. Ranking of solvents based on their performance index.

BT	MBT	DMBT	TMBT	DBT	MDBT	DM DBT	Quin	Indo	Carba
MIM1	MIM22	MIM7	MIM7	MIM19	MIM22	DMA	SULFO	SULFO	DMF
MIM19	MIM5	MIM21	MIM21	MIM8	MIM5	MIM6	MIM1	DMSO	MIM19
MIM8	MIM6	MIM20	MIM20	MIM3	NMP	MIM21	MIM18	MIM1	MIM8
MIM18	MIM4	MIM6	MIM11	MIM1	MIM6	MIM20	DMSO	MIM18	MIM2
MIM3	MIM2	MIM11	MIM6	DMF	MIM14	MIM11	MIM19	MIM17	Furfu
MIM2	MIM14	MIM5	MIM9	MIM2	DMA	MIM7	MIM8	MIM15	MIM3
MIM12	MIM21	MIM22	MIM10	MIM12	MIM4	MIM10	MIM17	MIM19	MIM4
MIM17	MIM13	MIM10	MIM13	MIM17	MIM2	NMP	MIM15	MIM8	MIM12
MIM4	MIM3	MIM13	DMA	MIM4	MIM13	MIM9	MIM12	MIM12	DMSO
MIM15	MIM7	MIM9	MIM5	MIM18	DMF	MIM5	MIM3	MIM3	MIM17
SULFO	MIM8	DMA	MIM22	Furfu	Furfu	MIM13	MIM2	DMF	MIM1
MIM14	MIM19	MIM14	NMP	MIM15	MIM10	MIM22	MIM16	MIM16	MIM14
MIM16	MIM10	MIM4	MIM14	DMSO	MIM9	MIM14	MIM4	MIM2	MIM16
MIM22	MIM20	NMP	MIM4	MIM16	MIM3	MIM4	DMF	Furfu	MIM15
MIM5	MIM9	MIM2	MIM2	MIM14	MIM16	MIM2	Furfu	MIM4	MIM22
DMSO	MIM11	MIM3	MIM16	MIM22	MIM8	Furfu	MIM14	MIM14	MIM18
MIM6	MIM12	MIM16	MIM3	MIM5	MIM19	DMF	MIM22	MIM22	MIM5
DMF	MIM16	MIM8	Furfu	SULFO	MIM12	MIM16	MIM5	MIM5	NMP
Furfu	MIM17	MIM19	DMF	NMP	MIM20	MIM3	NMP	NMP	MIM6
MIM13	NMP	MIM12	MIM8	MIM13	MIM11	MIM8	MIM13	MIM13	MIM13
MIM10	MIM15	Furfu	MIM19	MIM6	MIM21	MIM12	MIM6	MIM6	DMA
MIM9	MIM1	DMF	MIM12	DMA	MIM17	MIM19	MIM10	MIM10	SULFO
NMP	DMA	MIM17	MIM17	MIM10	MIM15	MIM17	MIM9	DMA	MIM10
MIM20	Furfu	MIM15	MIM15	MIM9	MIM7	MIM15	DMA	MIM9	MIM9
MIM21	MIM18	MIM1	MIM1	MIM11	MIM1	MIM1	MIM11	MIM11	MIM20
MIM11	DMF	MIM18	MIM18	MIM20	MIM18	MIM18	MIM20	MIM20	MIM11
MIM7	DMSO	DMSO	DMSO	MIM21	DMSO	DMSO	MIM21	MIM21	MIM21
DMA	SULFO	SULFO	SULFO	MIM7	SULFO	SULFO	MIM7	MIM7	MIM7

Table 3.12. Industrial usability index (S_{IUI}) with U_f=1 of solvents for sulfur and nitrogen compounds.

Solvent	BT	MBT	DMBT	TMBT	DBT	MDBT	DM DBT	Quin	Indo	Carba
DMF	3.07	1.53	0.69	0.26	4.46	2.17	1.04	8.87	18.60	3.15
Furfural	3.03	1.56	0.73	0.28	4.27	2.15	1.07	8.20	15.72	3.02
DMA	2.13	1.63	1.16	0.70	2.93	2.28	1.73	3.18	2.42	2.42
DMSO	3.61	1.12	0.31	0.07	4.19	1.28	0.37	17.90	93.25	2.88
NMP	2.44	1.67	1.05	0.55	3.36	2.30	1.54	4.32	4.30	2.61
SULFO	2.33	0.56	0.12	0.02	2.06	0.50	0.11	13.98	107.34	1.40
MIM1	3.03	0.98	0.29	0.07	2.68	0.86	0.27	11.87	48.02	1.72
MIM2	2.60	1.31	0.60	0.23	2.66	1.33	0.66	5.94	9.93	1.82
MIM3	2.64	1.22	0.51	0.18	2.69	1.23	0.55	6.82	13.82	1.80
MIM4	2.52	1.32	0.64	0.26	2.59	1.36	0.70	5.41	8.20	1.79
MIM5	2.18	1.39	0.82	0.41	2.19	1.43	0.91	3.49	3.35	1.65
MIM6	1.92	1.38	0.93	0.54	1.82	1.37	1.00	2.46	1.71	1.48
MIM7	1.37	1.21	1.04	0.82	0.98	1.00	0.93	1.06	0.36	1.03
MIM8	2.87	1.21	0.46	0.15	2.80	1.17	0.48	8.19	19.69	1.84
MIM9	1.56	1.14	0.79	0.47	1.61	1.24	0.92	2.04	1.42	1.33
MIM10	1.69	1.21	0.80	0.46	1.72	1.28	0.92	2.29	1.69	1.39
MIM11	1.39	1.14	0.88	0.60	1.26	1.11	0.94	1.42	0.69	1.15
MIM12	2.59	1.12	0.44	0.15	2.64	1.14	0.48	7.32	17.00	1.75
MIM13	1.78	1.23	0.79	0.43	1.84	1.31	0.91	2.58	2.09	1.45
MIM14	2.32	1.31	0.67	0.29	2.42	1.37	0.76	4.55	5.94	1.72
MIM15	2.45	0.99	0.36	0.11	2.55	1.02	0.40	7.76	21.28	1.68
MIM16	2.26	1.10	0.49	0.18	2.47	1.19	0.57	5.61	10.42	1.68
MIM17	2.59	1.05	0.38	0.12	2.62	1.05	0.41	8.04	21.71	1.72
MIM18	2.82	0.92	0.27	0.07	2.57	0.83	0.26	11.16	45.23	1.66
MIM19	2.89	1.21	0.46	0.15	2.82	1.17	0.48	8.37	20.51	1.85
MIM20	1.44	1.19	0.93	0.65	1.24	1.12	0.96	1.41	0.65	1.15
MIM21	1.44	1.23	1.01	0.76	1.12	1.07	0.96	1.23	0.48	1.10
MIM22	2.21	1.39	0.81	0.40	2.23	1.43	0.90	3.61	3.57	1.67

Table 3.13. Ranking of solvents based on their industrial usability index (S_{IUI}) with U_f=1.0.

BT	MBT	DMBT	TMBT	DBT	MDBT	DM DBT	Quin	Indo	Carba
DMSO	NMP	DMA	MIM7	DMF	NMP	DMA	DMSO	SULFO	DMF
DMF	DMA	NMP	MIM21	Furfu	DMA	NMP	SULFO	DMSO	Furfu
MIM1	Furfu	MIM7	DMA	DMSO	DMF	Furfu	MIM1	MIM1	DMSO
Furfu	DMF	MIM21	MIM20	NMP	Furfu	DMF	MIM18	MIM18	NMP
MIM19	MIM22	MIM20	MIM11	DMA	MIM22	MIM6	DMF	MIM17	DMA
MIM8	MIM5	MIM6	NMP	MIM19	MIM5	MIM21	MIM19	MIM15	MIM19
MIM18	MIM6	MIM11	MIM6	MIM8	MIM6	MIM20	Furfu	MIM19	MIM8
MIM3	MIM4	MIM5	MIM9	MIM3	MIM14	MIM11	MIM8	MIM8	MIM2
MIM2	MIM2	MIM22	MIM10	MIM1	MIM4	MIM7	MIM17	DMF	MIM3
MIM12	MIM14	MIM10	MIM13	MIM2	MIM2	MIM10	MIM15	MIM12	MIM4
MIM17	MIM21	MIM13	MIM5	MIM12	MIM13	MIM9	MIM12	Furfu	MIM12
MIM4	MIM13	MIM9	MIM22	MIM17	MIM10	MIM5	MIM3	MIM3	MIM17
MIM15	MIM3	Furfu	MIM14	MIM4	DMSO	MIM13	MIM2	MIM16	MIM1
NMP	MIM7	DMF	Furfu	MIM18	MIM9	MIM22	MIM16	MIM2	MIM14
SULFO	MIM8	MIM14	DMF	MIM15	MIM3	MIM14	MIM4	MIM4	MIM16
MIM14	MIM19	MIM4	MIM4	MIM16	MIM16	MIM4	MIM14	MIM14	MIM15
MIM16	MIM10	MIM2	MIM2	MIM14	MIM8	MIM2	NMP	NMP	MIM22
MIM22	MIM20	MIM3	MIM16	MIM22	MIM19	MIM16	MIM22	MIM22	MIM18
MIM5	MIM9	MIM16	MIM3	MIM5	MIM12	MIM3	MIM5	MIM5	MIM5
DMA	MIM11	MIM8	MIM8	SULFO	MIM20	MIM8	DMA	DMA	MIM6
MIM6	MIM12	MIM19	MIM19	MIM13	MIM11	MIM12	MIM13	MIM13	MIM13
MIM13	DMSO	MIM12	MIM12	MIM6	MIM21	MIM19	MIM6	MIM6	SULFO
MIM10	MIM16	MIM17	MIM17	MIM10	MIM17	MIM17	MIM10	MIM10	MIM10
MIM9	MIM17	MIM15	MIM15	MIM9	MIM15	MIM15	MIM9	MIM9	MIM9
MIM20	MIM15	DMSO	DMSO	MIM11	MIM7	DMSO	MIM11	MIM11	MIM20
MIM21	MIM1	MIM1	MIM1	MIM20	MIM1	MIM1	MIM20	MIM20	MIM11
MIM11	MIM18	MIM18	MIM18	MIM21	MIM18	MIM18	MIM21	MIM21	MIM21
MIM7	SULFO	SULFO	SULFO	MIM7	SULFO	SULFO	MIM7	MIM7	MIM7

Table 3.14. Ranking of solvents based on their industrial usability index (S_{IUI}) with U_f=0.8.

BT	MBT	DMBT	TMBT	DBT	MDBT	DM DBT	Quin	Indo	Carba
MIM1	MIM22	MIM7	MIM7	DMF	NMP	DMA	DMSO	SULFO	DMF
MIM19	MIM5	MIM21	MIM21	Furfu	DMA	NMP	SULFO	DMSO	Furfu
DMSO	MIM6	MIM20	MIM20	DMSO	DMF	MIM6	MIM1	MIM1	DMSO
MIM8	NMP	MIM6	MIM11	MIM19	Furfu	MIM21	MIM18	MIM18	NMP
MIM18	MIM4	DMA	DMA	MIM8	MIM22	MIM20	MIM19	MIM17	DMA
MIM3	MIM2	MIM11	MIM6	MIM3	MIM5	MIM11	MIM8	MIM15	MIM19
MIM2	MIM14	NMP	MIM9	NMP	MIM6	MIM7	MIM17	MIM19	MIM8
MIM12	DMA	MIM5	MIM10	MIM1	MIM14	MIM10	MIM15	MIM8	MIM2
MIM17	Furfu	MIM22	NMP	MIM2	MIM4	MIM9	MIM12	MIM12	MIM3
MIM4	MIM21	MIM10	MIM13	MIM12	MIM2	MIM5	DMF	DMF	MIM4
MIM15	MIM13	MIM13	MIM5	MIM17	MIM13	MIM13	MIM3	MIM3	MIM12
DMF	DMF	MIM9	MIM22	MIM4	MIM10	MIM22	Furfu	Furfu	MIM17
Furfu	MIM3	MIM14	MIM14	MIM18	MIM9	Furfu	MIM2	MIM16	MIM1
SULFO	MIM7	MIM4	MIM4	MIM15	MIM3	DMF	MIM16	MIM2	MIM14
MIM14	MIM8	MIM2	MIM2	MIM16	MIM16	MIM14	MIM4	MIM4	MIM16
MIM16	MIM19	Furfu	Furfu	MIM14	MIM8	MIM4	MIM14	MIM14	MIM15
MIM22	MIM10	DMF	DMF	DMA	MIM19	MIM2	MIM22	MIM22	MIM22
MIM5	MIM20	MIM3	MIM16	MIM22	MIM12	MIM16	MIM5	NMP	MIM18
NMP	MIM9	MIM16	MIM3	MIM5	MIM20	MIM3	NMP	MIM5	MIM5
MIM6	MIM11	MIM8	MIM8	SULFO	MIM11	MIM8	MIM13	MIM13	MIM6
MIM13	MIM12	MIM19	MIM19	MIM13	MIM21	MIM12	DMA	DMA	MIM13
DMA	MIM16	MIM12	MIM12	MIM6	MIM17	MIM19	MIM6	MIM6	SULFO
MIM10	MIM17	MIM17	MIM17	MIM10	MIM15	MIM17	MIM10	MIM10	MIM10
MIM9	MIM15	MIM15	MIM15	MIM9	DMSO	MIM15	MIM9	MIM9	MIM9
MIM20	MIM1	MIM1	MIM1	MIM11	MIM7	DMSO	MIM11	MIM11	MIM20
MIM21	MIM18	MIM18	MIM18	MIM20	MIM1	MIM1	MIM20	MIM20	MIM11
MIM11	DMSO	DMSO	DMSO	MIM21	MIM18	MIM18	MIM21	MIM21	MIM21
MIM7	SULFO	SULFO	SULFO	MIM7	SULFO	SULFO	MIM7	MIM7	MIM7

Table 3.15. Ranking of solvents based on their industrial usability index (S_{IUI}) with U_f=1.2.

BT	**MBT**	**DMBT**	**TMBT**	**DBT**	**MDBT**	**DM DBT**	**Quin**	**Indo**	**Carba**
DMSO	NMP	DMA	DMA	DMF	NMP	DMA	DMSO	DMSO	DMF
DMF	DMA	NMP	MIM7	Furfu	DMA	NMP	SULFO	SULFO	Furfu
Furfu	Furfu	MIM7	MIM21	DMSO	DMF	Furfu	MIM1	MIM1	DMSO
MIM1	DMF	MIM21	NMP	NMP	Furfu	DMF	MIM18	MIM18	NMP
NMP	MIM22	MIM20	MIM20	DMA	DMSO	MIM6	DMF	DMF	DMA
MIM19	MIM5	MIM6	MIM11	MIM19	MIM22	MIM21	Furfu	MIM17	MIM19
MIM8	MIM6	MIM11	MIM6	MIM8	MIM5	MIM20	MIM19	MIM15	MIM8
MIM18	DMSO	Furfu	MIM9	MIM3	MIM6	MIM11	MIM8	MIM19	MIM2
MIM3	MIM4	DMF	MIM10	MIM1	MIM14	MIM7	MIM17	MIM8	MIM3
MIM2	MIM2	MIM5	MIM13	MIM2	MIM4	MIM10	MIM15	Furfu	MIM4
MIM12	MIM14	MIM22	MIM5	MIM12	MIM2	MIM9	MIM12	MIM12	MIM12
MIM17	MIM21	MIM10	MIM22	MIM17	MIM13	MIM5	MIM3	MIM3	MIM17
DMA	MIM13	MIM13	Furfu	MIM4	MIM10	MIM13	MIM2	MIM16	MIM1
MIM4	MIM3	MIM9	DMF	MIM18	MIM9	MIM22	MIM16	MIM2	MIM14
MIM15	MIM7	MIM14	MIM14	MIM15	MIM3	MIM14	MIM4	MIM4	MIM16
SULFO	MIM8	MIM4	MIM4	MIM16	MIM16	MIM4	NMP	MIM14	MIM15
MIM14	MIM19	MIM2	MIM2	MIM14	MIM8	MIM2	MIM14	NMP	MIM22
MIM16	MIM10	MIM3	MIM16	MIM22	MIM19	MIM16	DMA	MIM22	MIM18
MIM22	MIM20	MIM16	MIM3	MIM5	MIM12	MIM3	MIM22	MIM5	MIM5
MIM5	MIM9	MIM8	MIM8	SULFO	MIM20	MIM8	MIM5	DMA	MIM6
MIM6	MIM11	MIM19	MIM19	MIM13	MIM11	MIM12	MIM13	MIM13	MIM13
MIM13	MIM12	MIM12	MIM12	MIM6	MIM21	MIM19	MIM6	MIM6	SULFO
MIM10	MIM16	MIM17	MIM17	MIM10	MIM17	DMSO	MIM10	MIM10	MIM10
MIM9	MIM17	DMSO	MIM15	MIM9	MIM15	MIM17	MIM9	MIM9	MIM9
MIM20	MIM15	MIM15	DMSO	MIM11	MIM7	MIM15	MIM11	MIM11	MIM20
MIM21	MIM1	MIM1	MIM1	MIM20	MIM1	MIM1	MIM20	MIM20	MIM11
MIM11	MIM18	MIM18	MIM18	MIM21	MIM18	MIM18	MIM21	MIM21	MIM21
MIM7	SULFO	SULFO	SULFO	MIM7	SULFO	SULFO	MIM7	MIM7	MIM7

It can be seen that as the weightage to complexity in solvent recovery increase, preference to chose the conventional organic solvents having boiling point less than gas oil increases.

The 4,6 DMDBT and quinoline are most refractive sulfur and nitrogen compound selected in the study. For easy understanding of the study results, the solvent ranking based on all the indexes scale for 4,6 DMDBT and quinoline is given in Table 3.16. There is no single solvent which seems the best for all the indexes. The C_i showed MIM7, S_{ij} showed sulfolane, P_I and S_{IUI} showed DMA as the best solvent for removal of 4,6 DMDBT from gas oil. C_i showed MIM6, S_{ij} and P_I showed sulfolane, and S_{IUI} showed DMSO are the best solvents for removal of quinoline.

Further, in commercial process there will always be slight loss of solvent and expenditure required for its makeup in the process would also increase the operating cost significantly. There is also reasonable amount of solvent stored as an inventory in the plant. Considering above, the price of solvent parameter could also be included in the estimation of S_{IUI}. The cost of conventional solvents which are used in the industry is almost comparable. However, cost of IL given in open literature are not true representative of their price as they are manufactured in very small quantity for either specific use or for lab scale utilization. The price of ILs may reduces drastically when they will be produced in bulk and their production technologies will get more mature. Hence, cost index of solvent has not been included in S_{IUI} in present study.

Still in light of the current price of IL and conventional solvents, the number of conventional solvents among top 5 solvents based on C_i, S_{ij}, P_I and S_{IUI} are 0, 2, 1 and 4, respectively, for 4,6 DMDBT removal; and 0, 2, 2 and 3 for quinoline removal. It is important to note that on S_{IUI} scale, DMA ranked 1st and 20th for 4,6 DMDBT and quinoline removal, DMSO solvent ranked 25th and 1st for 4,6 DMDBT and quinoline removal. DMF is the only solvent which is common among the top five solvents for 4,6 DMDBT and quinoline. Overall, DMF and DMA seem to be the best solvents for simultaneous desulfurization and denitrogenation of gas oil.

In this study, relationship between rankings and various parameters such as van der Waals volume, molar volume and solubility parameters was also explored.

Table 3.16. Rating of top 15 solvents based on selected indexes (C_i, S_{ij}, P_I and S_{IUI}) for 4,6 DMDBT and quinoline removal from gas oil.

4,6 DMDBT						Quinoline					
C_i	**S_{ij}**	**P_I**	**S_{IUI} U_I=0.8**	**S_{IUI} U_I=1.0**	**S_{IUI} U_I=1.2**	**C_i**	**S_{ij}**	**P_I**	**S_{IUI} U_I=0.8**	**S_{IUI} U_I=1.0**	**S_{IUI} U_I=1.2**
MIM7	SULFO	DMA	DMA	DMA	DMA	MIM6	SULFO	SULFO	DMSO	DMSO	DMSO
MIM21	DMSO	MIM6	NMP	NMP	NMP	MIM7	DMSO	MIM1	SULFO	SULFO	SULFO
MIM20	MIM18	MIM21	MIM6	Furfu	Furfu	MIM21	MIM1	MIM18	MIM1	MIM1	MIM1
MIM11	MIM1	MIM20	MIM21	DMF	DMF	MIM20	MIM18	DMSO	MIM18	MIM18	MIM18
MIM6	MIM15	MIM11	MIM20	MIM6	MIM6	MIM5	MIM15	MIM19	MIM19	DMF	DMF
DMA	MIM17	MIM7	MIM11	MIM21	MIM21	MIM22	MIM17	MIM8	MIM8	MIM19	Furfu
MIM9	MIM19	MIM10	MIM7	MIM20	MIM20	MIM11	MIM19	MIM17	MIM17	Furfu	MIM19
MIM10	MIM8	NMP	MIM10	MIM11	MIM11	MIM10	MIM8	MIM15	MIM15	MIM8	MIM8
MIM13	DMF	MIM9	MIM9	MIM7	MIM7	MIM13	MIM12	MIM12	MIM12	MIM17	MIM17
MIM5	MIM12	MIM5	MIM5	MIM10	MIM10	MIM9	MIM3	MIM3	DMF	MIM15	MIM15
MIM22	Furfural	MIM13	MIM13	MIM9	MIM9	MIM14	DMF	MIM2	MIM3	MIM12	MIM12
NMP	MIM3	MIM22	MIM22	MIM5	MIM5	DMA	MIM16	MIM16	Furfu	MIM3	MIM3
MIM14	MIM16	MIM14	Furfu	MIM13	MIM13	MIM4	Furfu	MIM4	MIM2	MIM2	MIM2
MIM4	MIM2	MIM4	DMF	MIM22	MIM22	MIM2	MIM2	DMF	MIM16	MIM16	MIM16
MIM2	MIM4	MIM2	MIM14	MIM14	MIM14	NMP	MIM4	Furfu	MIM4	MIM4	MIM4

No relationship was obtained between various rankings (based on capacity, selectivity, P_I and S_{IUI}) of solvents for removal of benzothiophene, DBT and their alkylated derivatives sulfur compounds, quinoline, indole and carbazole nitrogen compounds with respect to van der Waals volume and molar volume. When solubility parameter of all solvents (six conventional solvents and twenty two imidazolium based ionic liquids solvents) was correlated with the various rankings of solvents, again no trend was observed. However, when conventional and ILs solvent were categorized and correlated separately for 4,6 DMDBT sulfur compound removal with respect to rankings based on selectivity and capacity, a linear trend (as suggested by the reviewer) was observed. It was found that the selectivity and solubility parameter follow same trend whereas solubility parameter of solvent and its capacity have exactly opposite trend. Thus, rankings based on selectivity and capacity correlated well with the solubility parameter. Since, P_I and S_{IUI} represent the combined effect, no trend was observed for these rankings.

In a study (detail study given in chapter 4) used various solvents namely acetonitrile (ACN), DMF, furfural, DMA and DMSO were used for extraction of sulfur and polyaromatic impurities from actual straight run gas oil (SRGO) containing 1.3 wt.%. sulfur. Performance of solvent extraction process was evaluated in terms of a P_f which was governed by degree of sulfur removal and yield of extracted SRGO (ESRGO). DMF was found to be the best solvent. In the present study also, DMF was found to be the best solvent for desulfurization of gas oil. This demonstrates that the screening strategy adopted in this work has high significance.

This study reveals that IL solvents may be preferred based on their individual capacity and selectivity values over lower boiling point conventional organic solvents for removal of sulfur compounds from gas oil. However, complexity in their recovery brings their ranking lower than the conventional organic solvents. This strongly suggests that ILs based solvents which can be very selective could have great chances in recovery of pure aromatic extraction which are to be vaporized for solvent recovery and small scale, pharmaceutical, specific chemical manufacturing industries where the quality of product is of predominant importance and even small loss of product can overcome the additional expenditure involved in its recovery.

Chapter – 4

DESULFURIZATION OF STRAIGHT RUN GAS OIL

4.1. GENERAL

This chapter presents experimental evaluation of performance of industrially proven and viable solvents namely acetonitrile (ACN), N-N-dimethyl formamide (DMF), furfural N-N-dimethyl acetamide (DMA) and dimethyl sulfoxide (DMSO) for removal of sulfur compounds from straight run gas oil (SRGO) containing high sulfur content (1.3 wt.%). Effect of extraction temperature (T_E), solvent to feed (S/F) ratio, anti-solvent (water) concentration (and number of stages on the degree of sulfur and aromatics removal and yield were evaluated in batch extraction system.

Packed bed extractor is generally used in commercial extraction process. Therefore, operating parameter optimization for desulfurization of gas oil in continuous counter current packed bed extractor will enhance the confidence of an industrialist about the operational process flexibilities and capabilities and also provides the true insight of the process to entrepreneur for its implementation in industry. In view of this, initially, five experimental runs were carried out using the two different temperatures and 5 different W_c in main solvent in packed bed extractor. Subsequently, a full factorial central composite design (CCD) has been used to design the experiments with two responses namely, yield of ESRGO and sulfur removal for operating conditions optimization. Three operational parameters namely water concentration (W_c) in main solvent, solvent to feed ratio (S/F) and T_E were used as input variables for desulfurization of SRGO using DMF as solvent. Multi-response optimization with desirability function approach was used to maximize sulfur removal (D_{sr}) and yield (Y) of extracted SRGO (ESRGO). To improve the feasibility of extractive desulfurization process implementation in the industry, various options for extract value addition and its utilization were identified and discussed from industrial point of view in detail.

4.2. 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 (Petkov et al., 2004; Gaile et al., 2006; Toteva et al., 2007; Gaile, 2008; El-Aty et al., 2009; Hassan et al., 2009; Gaile et al., 2010a,b). 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 (Rawat et al., 1972; Rawat and Gulati, 1976; Hampe, 1985; Cusack et al., 1991; Cusack et al., 1991; Ghosh, 1993).

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 zeotrope 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 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 (ε_S) for sulfur, sulfur distribution coefficient (K_s), yield (Y) of extracted gas oil, degree of sulfur removal (D_{sr}), and performance factor ($P_{f,\alpha}$).

Extraction factor (ε_S) is used to represent the capacity of solvent. For single stage solvent extraction, it is defined as (Alders, 1959):

$$\varepsilon_s = \frac{\text{Quantity of component i in the extract phase}}{\text{Quantity of component i in the raffinate phase}} \tag{4.1}$$

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:

$$K_s = y_S / x_S \tag{4.2}$$

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:

$$\text{Yield}\left(\%\right) = \frac{\text{Volume of solvent free ESRGO}}{\text{Volume of SRGO}} \times 100 \tag{4.3}$$

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:

$$F = R + E \tag{4.4}$$

$$x_{f,i} F = x_{r,i} R + x_{e,i} E \tag{4.5}$$

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}) was estimated using the following expression:

$$D_{sr} = \frac{\left(S_{SRGO} - S_{ESRGO}\right)}{S_{SRGO}} \times 100 \tag{4.6}$$

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 (D_{ar}) was calculated by the following expression:

$$D_{ar,i} = \frac{\left(A_{SRGO,i} - A_{ESRGO,i}\right)}{A_{SRGO,i}} \times 100 \tag{4.7}$$

where, $A_{SRGO,i}$ and $A_{ESRGO,i}$ 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 D_{sr} and aromatic compounds (Otsuki et al., 2000). 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 ($P_{f,\alpha}$) of solvent is defined as:

$$P_{f,\alpha} = \alpha D_{sr} + (1-\alpha) \times Yield(\%) \tag{4.8}$$

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

4.3. EXPERIMENTAL

4.3.1. Materials

Straight run gas oil (SRGO) was obtained from an Indian refinery. Physicochemical properties of SRGO are given in Table 4.1. ACN (99.5%+: MERCK), DMF (99.5%, MERCK), furfural (98%: SD Fines), DMA (99.5%+: MERCK) and 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. Solid ammonium sulphate and anhydrous calcium chloride was used to remove water from hydrocarbon phase.

4.3.2. 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. American standard testing method (ASTM) D86 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.

4.3.3. Experimental Design for Parameters Optimization

A full central composite design (CCD) with alpha value of 1.6817 was used to design the experiments. Three major process parameters (W_c, S/F and T_E) were selected based on preliminary runs carried out in packed bed extraction column and various run in single stage batch extraction system. The level of parameters was decided considering the effect of these parameters on sulfur removal and yield of ESRGO.

Table 4.1. 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 @ 20°C	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)
Initial boiling point (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
Final boiling point (FBP)	380.9
Distillate	97.0
Residue	2.5
Loss	0.5

The units of the selected major parameters differ from one another and were to be tested over different ranges. Therefore, the coding of these parameters was required so as to eliminate the effect of different unit and tested range of selected parameters on response. The parameters were coded so that effect of these parameters on the response is evenly distributed. For statistical calculations, these three main variables X_i (X_1: W_c, X_2: S/F, X_3: T_E) were coded so as to range from -1 to 1 (the same levels) using equation given below (Thakur et al., 2009):

$$X_i = \frac{x_i - \left(\left[x_{i,\max} + x_{i,\min}\right]/2\right)}{\left[x_{i,\max} - x_{i,\min}\right]/2} \tag{4.9}$$

where, x_i is the variable, X_i is the coded variable; x_{imax} and x_{imin} are the maximum and minimum values of the variable. Variables and their levels are given in Table 4.2.

Table 4.2. Variables and levels of the design model.

Variable, unit	**Factor**		**Range and level**	
	X	-1	0	1
Water concentration in solvent, (Volume%)	X_1	2	3.7	5.4
Solvent to feed ratio, S/F (ml/ml)	X_2	1	1.5	2.0
Extraction temperature, T (°C)	X_3	45	52.5	60

Design-expert trial version software was used to analyze the two responses, namely, yield of ESRGO (Y_1) and sulfur removal (Y_2). Total number of experiments required to find the optimized conditions for maximizing the responses, Y_1 and Y_2, were calculated using expression: No. of experiments= 2^n (factor points) + $2n$ (axial points) + 6 (center points). Where, n is number of process parameters which was taken as three. Though, estimated numbers of experiments were 20, however, only 19 experiments conducted as per the experimental design matrix (Table 2). Experiment in which W_c in solvent was corresponding to level of 1.683 could not be conducted due to problem in feed dispersion in solvent at feed inlet location. Independent parameters for different experiments runs are given in Table 4.3.

In the present study, both the responses, Y_1 and Y_2, were to be maximized. Multi-response optimization with desirability function approach was used to estimate the optimum value of operating parameters required to maximize the responses (Derringer and Suich, 1980). During the application of desirability function, each response, Y_i, was transformed to an individual desirability function d_i such that it varied in the range of 0 to 1.

Table 4.3. Independent parameters for different experiment run and corresponding responses.

Std order	run order	Water (volume%)	S/F	T (°C)	Yield of ESRGO (%)		Sulfur removal (%)	
		Values of variables			**Exp.**	**Pred.**	**Exp**	**Pred.**
1	7	2.00	1.00	45.0	84.1	84.5	51.5	49.9
2	16	5.40	1.00	45.0	90.3	90.2	33.8	34.4
3	18	2.00	2.00	45.0	76.1	76.4	64.6	68.1
4	9	5.40	2.00	45.0	85.5	86.2	47.7	48.3
5	6	2.00	1.00	60.0	80.7	80.0	57.7	57.6
6	19	5.40	1.00	60.0	83.2	83.0	49.2	46.3
7	10	2.00	2.00	60.0	73.8	74.0	70.8	70.8
8	11	5.40	2.00	60.0	81.5	81.2	53.1	55.3
9	17	0.84	1.50	52.5	74.0	73.9	72.3	71.5
10	13	3.70	0.80	52.5	85.9	86.4	38.5	42.0
11	14	3.70	2.34	52.5	79.2	78.7	63.8	60.6
12	4	3.70	1.50	40.0	88.4	87.8	50.0	48.5
13	1	3.70	1.50	65.0	79.3	79.9	60.0	60.7
14	15	3.70	1.50	52.5	82.7	83.0	57.7	57.0
15	3	3.70	1.50	52.5	82.6	83.0	57.7	57.0
16	8	3.70	1.50	52.5	83.6	83.0	56.9	57.0
17	12	3.70	1.50	52.5	84.3	83.0	56.2	57.0
18	5	3.70	1.50	52.5	82.9	83.0	56.9	57.0
19	2	3.70	1.50	52.5	82.1	83.0	57.7	57.0

The value of $d_i(Y_i)=0$ represents a completely undesirable value of Y_i and $d_i(Y_i)=1$ represents a completely desirable or ideal response value (Hu et al., 2008). The individual desirability used in the study to maximize the response is defined as:

$$d_i(Y_i)=\begin{cases} 0 & \text{if } Y_i(x)\le L_i \\ \left(\dfrac{Y_i(x)-L_i}{U_i-L_i}\right)^r & \text{if } L_i<Y_i(x)<U_i \\ 1 & \text{if } Y_i(x)\ge U_i \end{cases} \qquad (4.10)$$

where, L_i and U_i are the minimum and maximum acceptable value of response Y_i, and r is a weight factor and positive constant, used to vary the emphasis to the goal. The overall desirability *D* was obtained using geometric mean of individual desirability functions as follows:

$$D=(d_1\times d_2\times\ldots\times d_k)^{1/k}=(\prod_{i=1}^{k}d_i)^{1/k} \qquad (4.11)$$

where, $0 \le D \le 1$ and k is number of responses. In other words, maximum of the overall desirability can be determined by the simultaneous optimization of several responses.

4.3.4. Apparatus and Procedure

4.3.4.1. Batch single stage equilibrium extraction

A known amount of gas oil and solvent was charged in a jacketed glass mixer settler provided with a stirrer. T_E was maintained within ±0.5°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). The moisture of the solvent free raffinate was removed using the solid ammonium sulphate and anhydrous calcium chloride. Thereafter it was analyzed for its sulfur and aromatics concentration. Actual experimental set up used for single stage extraction is shown in Figure 4.1.

4.3.4.2. 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. Column was filled up to 140 mm of its height with

2.3 to 3.0 mm structured cannon packing. Settling zones of 15 mm were provided at the top and bottom of the column. Feed and solvent were pumped using the metering pumps at the bottom and top of the column, respectively. Flow rates of feed and solvent were fixed so as to get the desired solvent-to-feed ratio with the total flow rate of 6 ml/min. 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. Level of interface was kept constant in the settling zone at the top of the column during the run. Temperature of column was maintained by circulating the hot water in jacket of the column. 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. Gas oil raffinate phase and solvent rich extract phase were obtained from top and bottom of the column, respectively. Raffinate phase was further treated in the same way as in single stage equilibrium experiments. Actual experimental set up for continuous counter current extraction is shown in Figure 4.2, whereas schematic of experimental set up is given in Figure 4.3.

4.4. RESULTS AND DISCUSSION

4.4.1. Batch Equilibrium Extraction

4.4.1.1. 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^{o}C using procedure as described in section 4.3.4.1. Yields of ESRGO and D_{sr} were estimated using the equations 4.3 and 4.6, respectively. RI value of aromatic compounds is higher than the paraffinic materials. Lower value of RI of ESRGO indicates the higher removal of aromatics compounds.

Results (Table 4.4) clearly indicate that D_{sr} and yield of ESRGO using solvent extraction strongly depend on the type of solvent used. D_{sr} using DMF, DMA and furfural 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 economic point of view, maximum sulfur removal with maximum yield value is desirable.

Figure 4.1. Actual photograph of glass mixer-settler for single stage equilibrium extraction.

Figure 4.2. Picture of actual experimental set up for continuous counter current extraction.

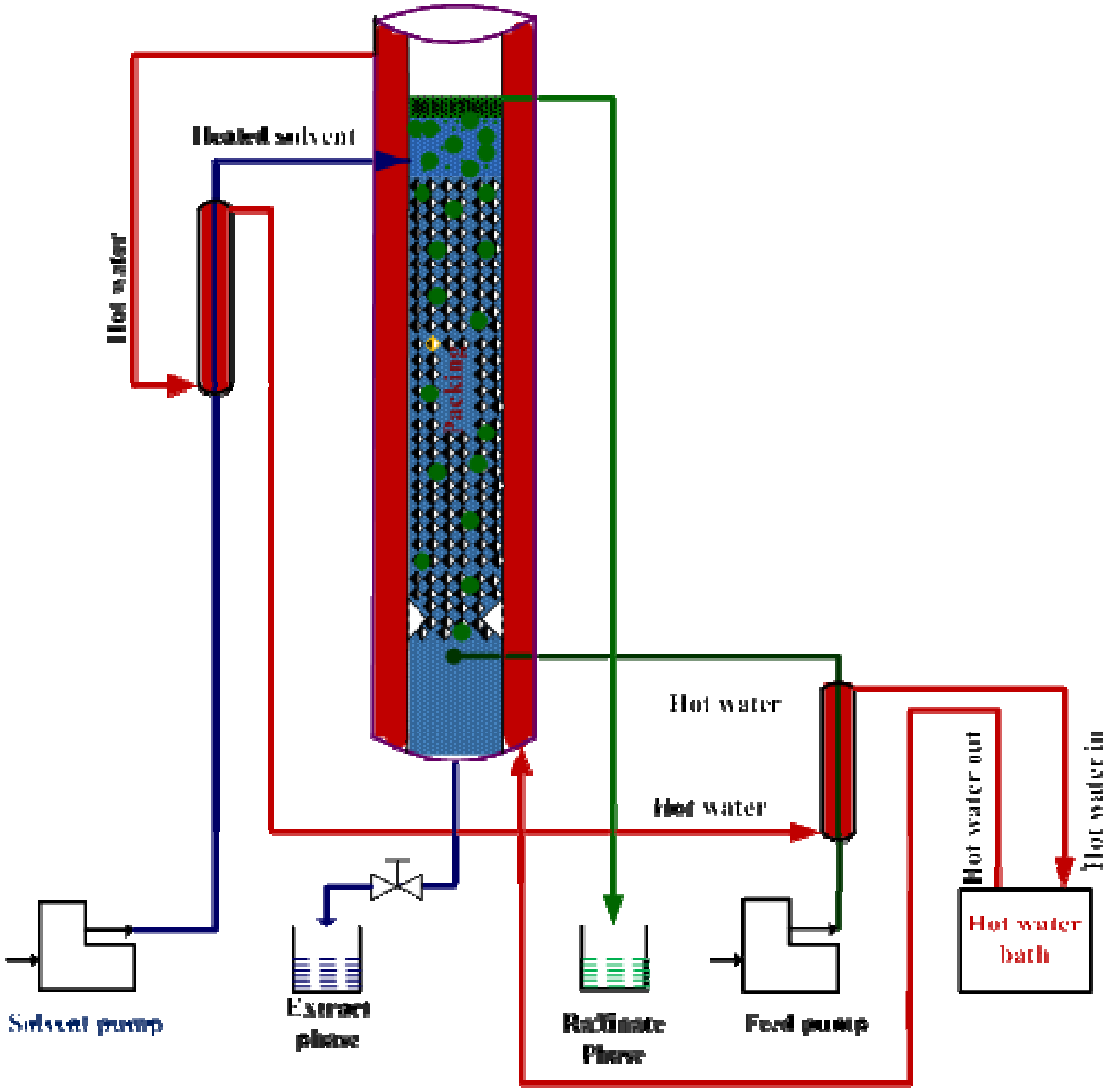


Figure 4.3. Schematic of experimental set up for continuous counter current extraction.

Considering this, $P_{f,\alpha}$ for each solvent was estimated using the equation 4.8 using weight factor (α)=0.5, thus giving equal importance to yield and D_{sr}. The values of $P_{f,0.5}$ are given in Table 4.4. It is observed that when the sulfur removal and yield were assigned the same value of α, values of $P_{f,\alpha}$ follow the order: furfural > DMF > DMA > DMSO > ACN.

ε_S and K_S follow the order: DMA > DMF > furfural > DMSO > ACN. However, the values of ε_S for DMF and furfural are comparable, whereas for $K_{S,}$ there is significant difference. It may be attributed to the difference in density of solvents.

Effect of the value of α (in the range of 0.3-0.9) on the $P_{f,\alpha}$ value for each solvent is shown in Figure 4.4. It is clear that $P_{f,\alpha}$ 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 $P_{f,\alpha}$ are always much less as compared to other solvents at all values of α. $P_{f,\alpha}$ values of DMF are higher than that of DMA for $\alpha < 0.7$, however for $\alpha \geq 0.7$, $P_{f,\alpha}$ values of DMA become higher than that of DMF.

Table 4.4. 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°C (gm/cm^3)	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

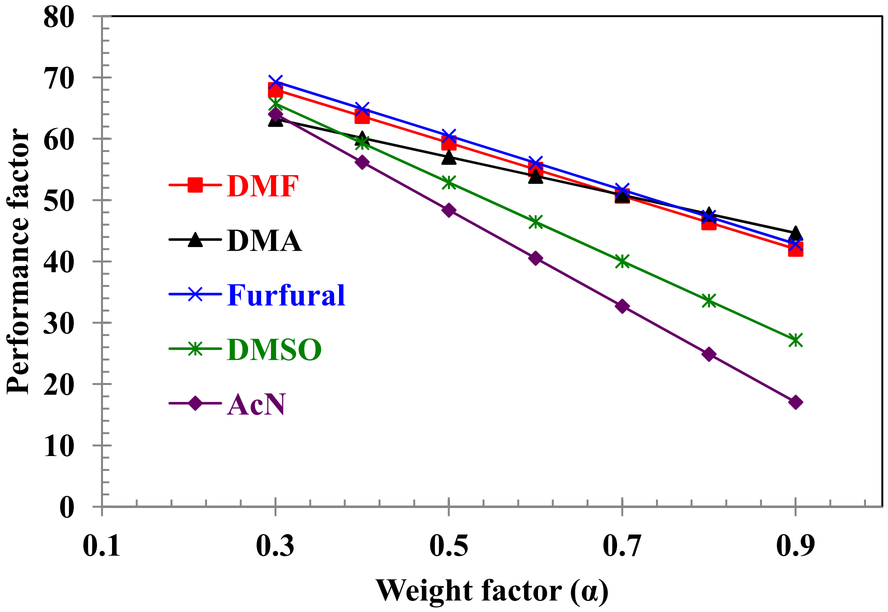


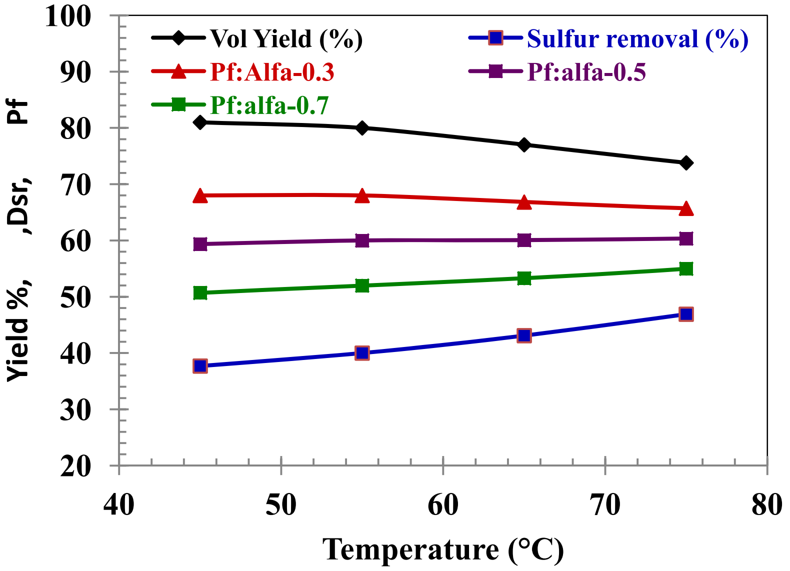
Figure 4.4. Effect of weight (α) on solvent's performance factor ($P_{f,\alpha}$) during extractive desulfurization of SRGO by various solvents.

$P_{f,\alpha}$ 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 $P_{f,\alpha}$ for whole range of α.

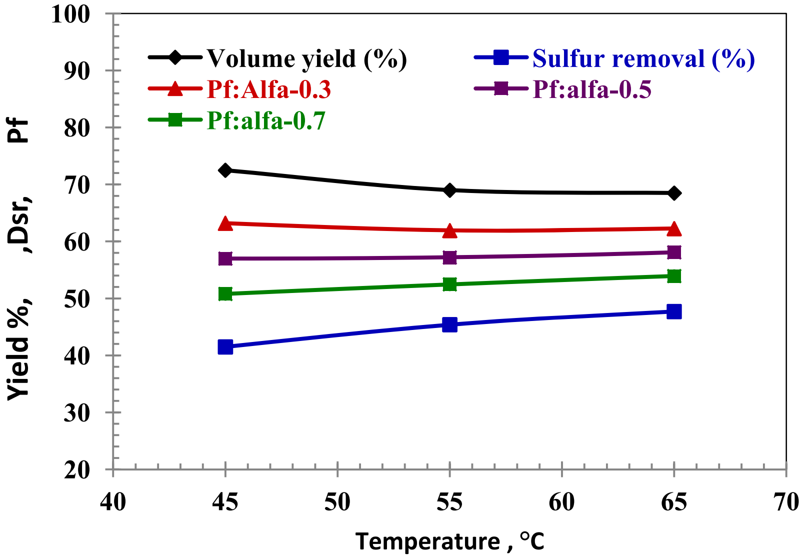
However, considering the low oxidative and thermal stability of furfural as reported in literature (Sharma et al., 2013), lower values of ε_s and distribution coefficient, DMF and DMA were selected as solvents for further study.

4.4.1.2. Effect of extraction temperature and water concentration

It is well known that T_E 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 4.5. 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 4.5 that an increase in the T_E 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.

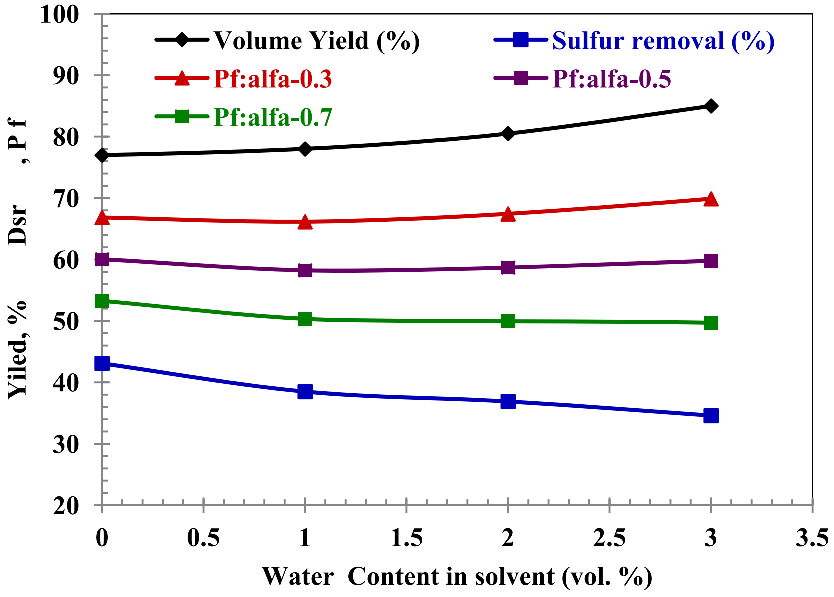


(a) DMF

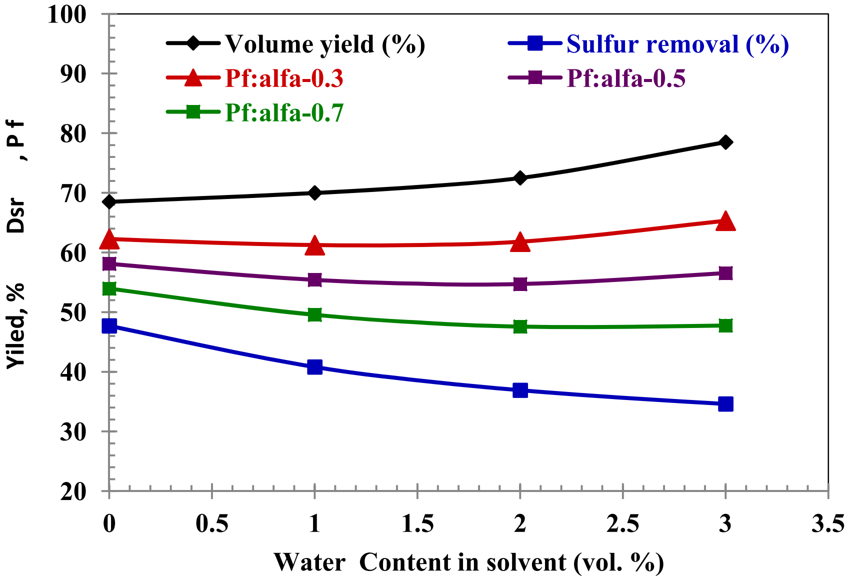


(b) DMA

Figure 4.5. Effect of extraction temperature on volume yield, degree of sulfur removal (D_{sr}) and solvent's performance factor ($P_{f,\alpha}$) for S/F ratio of 1.



(a) DMF



(b) DMA

Figure 4.6. Effect of anti-solvent (water) concentration on volume yield, degree of sulfur removal (D_{sr}) and performance factor ($P_{f,\alpha}$) for S/F ratio=1.0 and Temperature=65°C.

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 (Gaile et al., 2010). Considering this, extraction of SRGO with DMF and DMA solvents was carried out by varying the W_c in the range of 0-3.0 volume% at 65°C so as to understand their impact on D_{sr} and $P_{f,\alpha}$ of DMF and DMA. Results are shown in Figure 4.6. As expected, an increase in W_c in the solvent, increased the ESRGO yield, however, it also decreased the D_{sr} 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 an increase in W_c in solvent. $P_{f,\alpha}$ values of DMA solvent are lower than that of DMF over whole range of temperature and W_c studied. It can be inferred that when D_{sr} is more important than yield, it is better to do the extraction at higher temperature and lower W_c and vice versa. It may be noted that $P_{f,\alpha}$ values for DMF are higher than the DMA values for $\alpha \leq 0.7$.

Considering the significance of ESRGO yield and D_{sr} 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^{o}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.

4.4.1.3. Effect of ratio (S/F)

In this study, SRGO was extracted with DMF solvent at the temperature of 65 ˚C and with volumetric S/F ratio of 1.0, 1.5, 2.0, and 3.0 using single stage equilibrium extractor. Results are shown in Figure 4.7. It is observed that sulfur removal increased with an increase the S/F ratio, whereas, the ESRGO yield decreased. $P_{f,0.5}$ values are nearly constant up to S/F ratio of 2.0, however, it decreases with an increase in S/F ratio beyond 2. It is important to note that energy and capital requirement of the extraction process also increases with an increase in S/F ratio. Hence, S/F ratio of 1.0 seems to be better for continuous extraction.

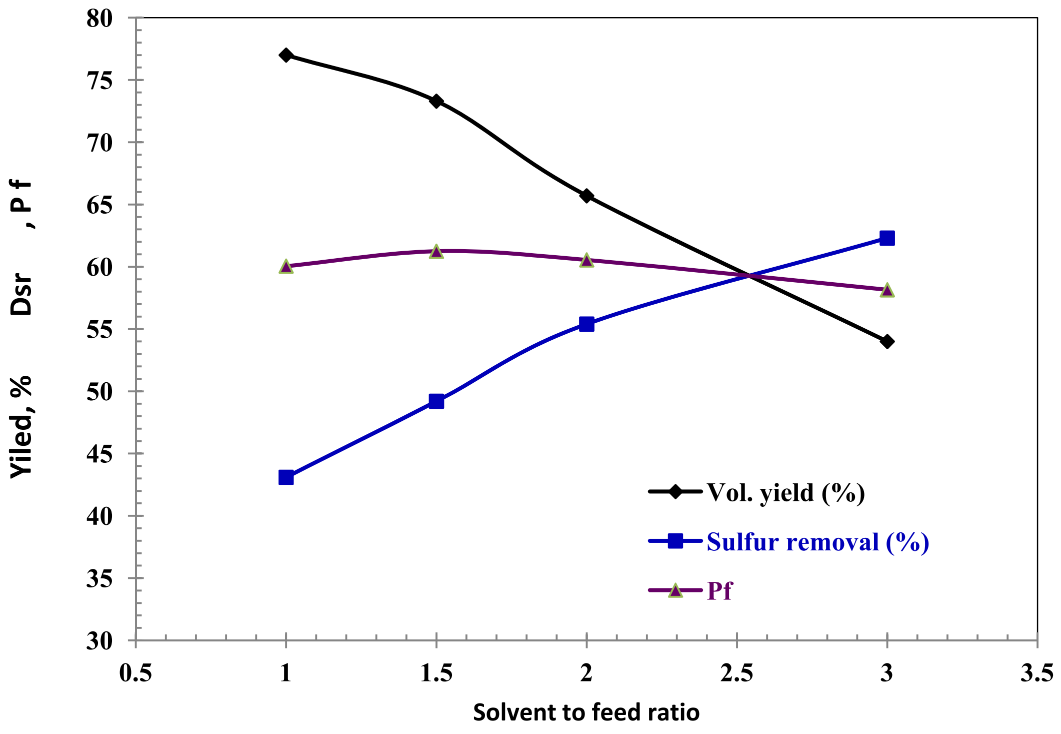


Figure 4.7. Effect of S/F ratio on volume yield%, degree of sulfur removal (D_{sr}) and solvent's performance factor ($P_{f,\alpha}$) for batch extraction using DMF as solvent for α=0.5 and temperature=65°C.

4.4.1.4. 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 T_E 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. 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. Results obtained for all three stage extractions are given in Table 4.5.

Table 4.5. 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 ($P_{f,\alpha}$)	59.3	52.4	55.1

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 D_{sr} at the expense of lower yield value of ESRGO using multistage solvent extraction. $P_{f,\alpha}$ (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.

4.4.2. Preliminary Experiments in Packed Bed Extractor

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 45°C to 55°C and W_c in solvent from 0.0 to 5.0%. Four cases were formed by selecting the two values for each temperature and W_c in solvent. The analysis of ESRGO obtained for these four cases, one batch extraction case and SRGO has been summarized in Table 4.6. The code of different runs along with experimental conditions is also given in Table 4.6. 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 D_{sr} are shown in Figure 4.8.

It may be seen in Table 4.6 and Figure 4.8 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 (Ismagilov et al., 2011).

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

$P_{f,\alpha}$ values for each case were estimated with the different α values to understand the overall impact of T_E and W_c on solvent extraction process. Results are shown in Figure 4.9. 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 $P_{f,\alpha}$ values is least as the sulfur removal and yield number are close to each other.

Table 4.6. 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 ($P_{f,\alpha}$)		31.0	53.2	50.5	42.3	34.7

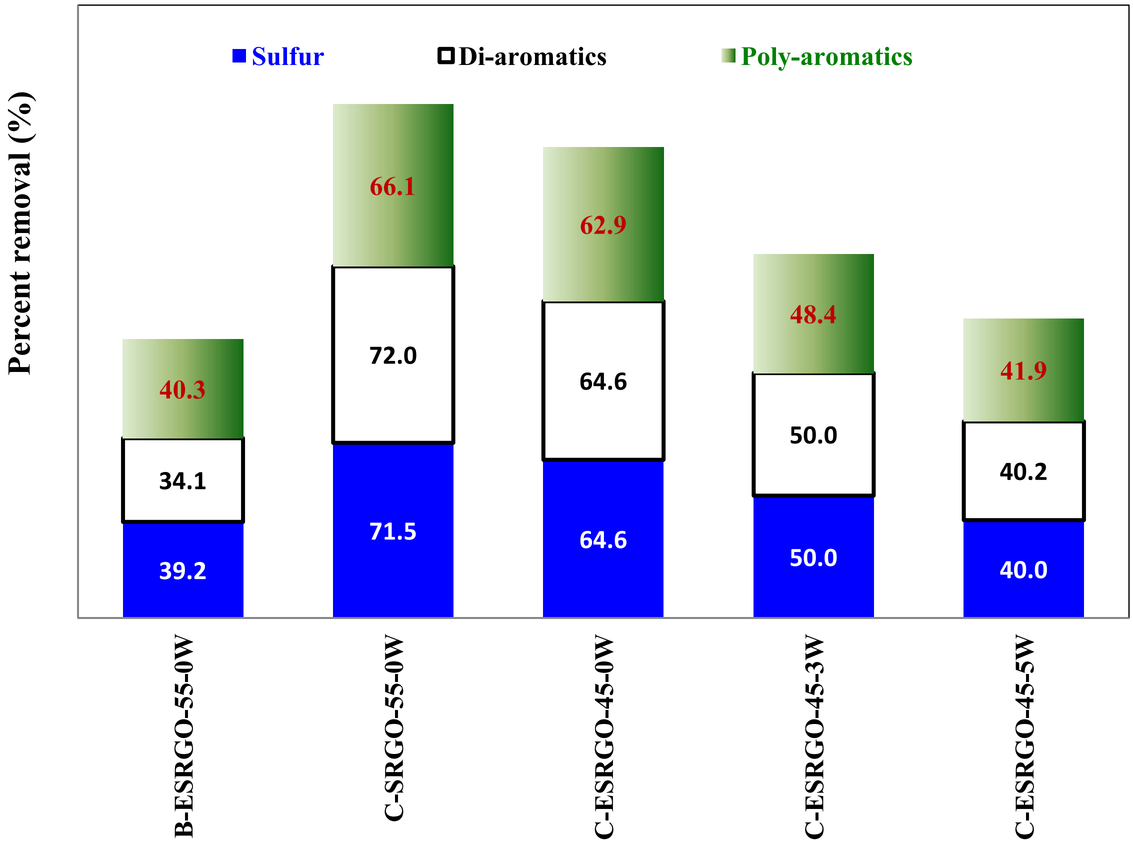


Figure 4.8. Comparative analysis of degree of sulfur, di-aromatics and poly-aromatics removal during batch and continuous extraction using DMF as solvent at various experimental conditions.

It may clearly be seen that decrease in the T_E spreads the $P_{f,\alpha}$ values i.e. there is large variation in $P_{f,\alpha}$ values for various α values ($P_{f,0.3}$=68.7 to $P_{f,0.7}$=74.1). Similarly, an increase in W_c increases the spread of $P_{f,\alpha}$ values. For C-ESRGO-45T-3W case (T_E=45 and W_c=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 $P_{f,\alpha}$ 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, $P_{f,\alpha}$ values decreases with an increase in water content and decrease in temperature.

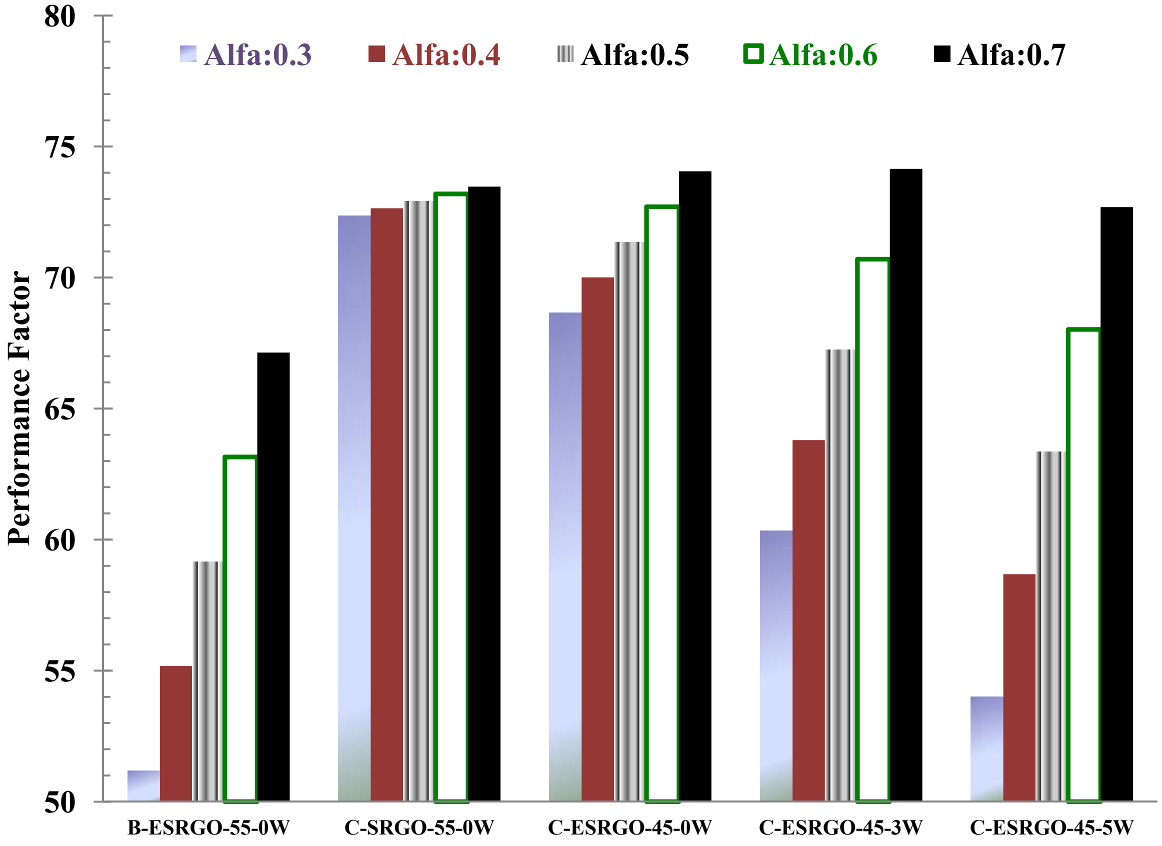


Figure 4.9. Effect of weight factor (α) on solvent's performance factor ($P_{f,\alpha}$) during batch and continuous extraction using DMF as solvent at various experimental conditions.

4.4.3. Optimization

4.4.3.1. Statistical analysis of model

Values of yield of ESRGO (Y_1) and degree of sulfur removal (Y_2) were measured according to the experimental conditions specified in design matrix and the results are given in Table 4.3. Adequacy of the models used is given in Table 4.7. For both the responses, cubic model was found to be aliased and quadratic model which includes independent variables and their interactions was suggested. Quadratic model shows the maximum value of determined R^2, adjusted R^2 and predicted R^2 except cubic model which was aliased. This implies a good correlation between observed and predicted values for quadratic model. Analysis of variance (ANOVA) of quadratic model for both the responses, Y_1 and Y_2, is given in Table 4.8. F value, Prob > F value, determined R^2 and adjusted R^2 for response Y_1 were found to be: 57.32, < 0.0001, 0.98, and 0.97, respectively. Respective values for response Y_2 were: 26.89, < 0.0001, 0.96 and 0.93. These values indicate that quadratic model is statistically highly significant for both the responses. Further, the values of Prob > F less than 0.05 indicates that model term is significant. The results shown in Table 4.7 reveal that W_c, S/F, T_E, and $W_c{}^2$ model terms are highly significant, whereas, W_c - S/F, W_c-T_E are significant for Y_1. In model for Y_2, the W_c, S/F, T_E terms are highly significant, whereas, S/F^2 is significant term. Adeq Precision parameter is used to understand the applicability of model to to navigate the design space. It measures the signal to noise ratio. A ratio greater than 4 is desirable. In the present study, signal to noise ratio values for Y_1 for Y_2 were 28.03 and 20.12, respectively. These values are significantly higher than 4.0 indicating adequate signal strength to investgate the design space.

Quadratic model equations in term of coded parameters for response Y_1 and Y_2 are given below:

$$\text{Yield\% } (Y_1) = +82.99 + 3.21\times X_1 - 2.49\times X_2 - 2.37\times X_3 - 1.32\times X_1^2 - 0.036\times X_2^2 + 0.30\times X_3^2 + 1.05\times X_1\times X_2 - 0.68\times X_1\times X_3 + 0.54\times X_2\times X_3 \quad (4.12)$$

$$\text{Sulfur removal } (Y_2) = +57.02 - 7.77\times X_1 + 6.80\times X_2 + 3.67\times X_3 + 0.50\times X_1^2 - 2.79\times X_2^2 - 0.88\times X_3^2 - 1.06X_1\times X_2 + 1.06\times X_1\times X_3 - 1.25\times X_2\times X_3 \quad (4.13)$$

ANOVA analysis also reveals that W_c, S/F and T are significant parameters for both the responses. Experimental and predicted values of responses shown in Table 2 indicate that the residuals are minimum.

Table 4.7. Adequacy of the models tested for yield and sulfur removal.

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Rem-ark	Std. Dev.	R^2	Adjusted R^2	**Predicted R^2**	**PRESS**	Rem-arks
Yield												
Mean	128101.8	1	128101.81									
Linear	301.2	3	100.39	41.85	< 0.0001		1.55	0.89	0.87	0.80	67.58	
2FI	14.7	3	4.91	2.78	0.0869		1.33	0.94	0.91	0.75	84.51	
Quadratic	15.5	3	5.15	8.02	0.0065	SU	0.80	0.98	0.97	0.90	33.93	SU
Cubic	2.6	4	0.66	1.04	0.4695	AL	0.79	0.99	0.97		+	AL
Residual	3.2	5	0.63									
Total	128439.0	19	6759.95									
Sulfur removal												
Mean	58708.47	1	58708.47									
Linear	1447.33	3	482.44	41.08	< 0.0001		3.43	0.89	0.87	0.81	303.36	
2FI	30.40	3	10.13	0.83	0.5005		3.49	0.91	0.87	0.69	497.56	
Quadratic	87.53	3	29.18	4.51	0.0341	SU	2.54	0.96	0.93	0.62	612.42	SU
Cubic	56.24	4	14.06	35.64	0.0007	AL	0.63	1.00	1.00		+	AL
Residual	1.97	5	0.39									
Total	60331.95	19	3175.37									

*DF=Degree of freedom; SU=Suggested; AL=Aliased

Table 4.8. The ANOVA results for the second-order quadratic model fitted for ESRGO yield and sulfur removal.

		Yield					Sulfur removal				
Source	DF	Sum of Squares	Mean Square	F Value	Prob > F	Rem-arks	Sum of Squares	Mean Square	F Value	Prob > F	Rem-arks
Model	9	331.37	36.82	57.32	< 0.0001	HS	1565.27	173.92	26.89	< 0.0001	HS
A	1	91.49	91.49	142.43	< 0.0001	HS	535.55	535.55	82.79	< 0.0001	HS
B	1	77.06	77.06	119.98	< 0.0001	HS	576.31	576.31	89.10	< 0.0001	HS
C	1	76.18	76.18	118.61	< 0.0001	HS	182.54	182.54	28.22	0.0005	HS
A2	1	14.36	14.36	22.36	0.0011	S	2.04	2.04	0.32	0.588	
B2	1	0.01	0.01	0.02	0.8861		82.51	82.51	12.76	0.006	S
C2	1	1.17	1.17	1.83	0.2096		10.34	10.34	1.60	0.238	
AB	1	8.78	8.78	13.67	0.0049	S	8.95	8.95	1.38	0.2697	
AC	1	3.65	3.65	5.68	0.0411	S	8.95	8.95	1.38	0.2697	
BC	1	2.31	2.31	3.60	0.0902		12.50	12.50	1.93	0.1979	
Residual	9	5.78	0.64				58.22	6.47			
Lack of Fit	4	2.63	0.66	1.04	0.4695	NS	56.24	14.06	35.64	0.0007	S
Pure Error	5	3.15	0.63				1.97	0.39			
Cor Total	18	337.15					1623.48				

*DF=Degree of freedom; HS: highly significant; S=Significant; =Not significant

4.4.3.2. Effect of W_c, S/F, T_E on Y1

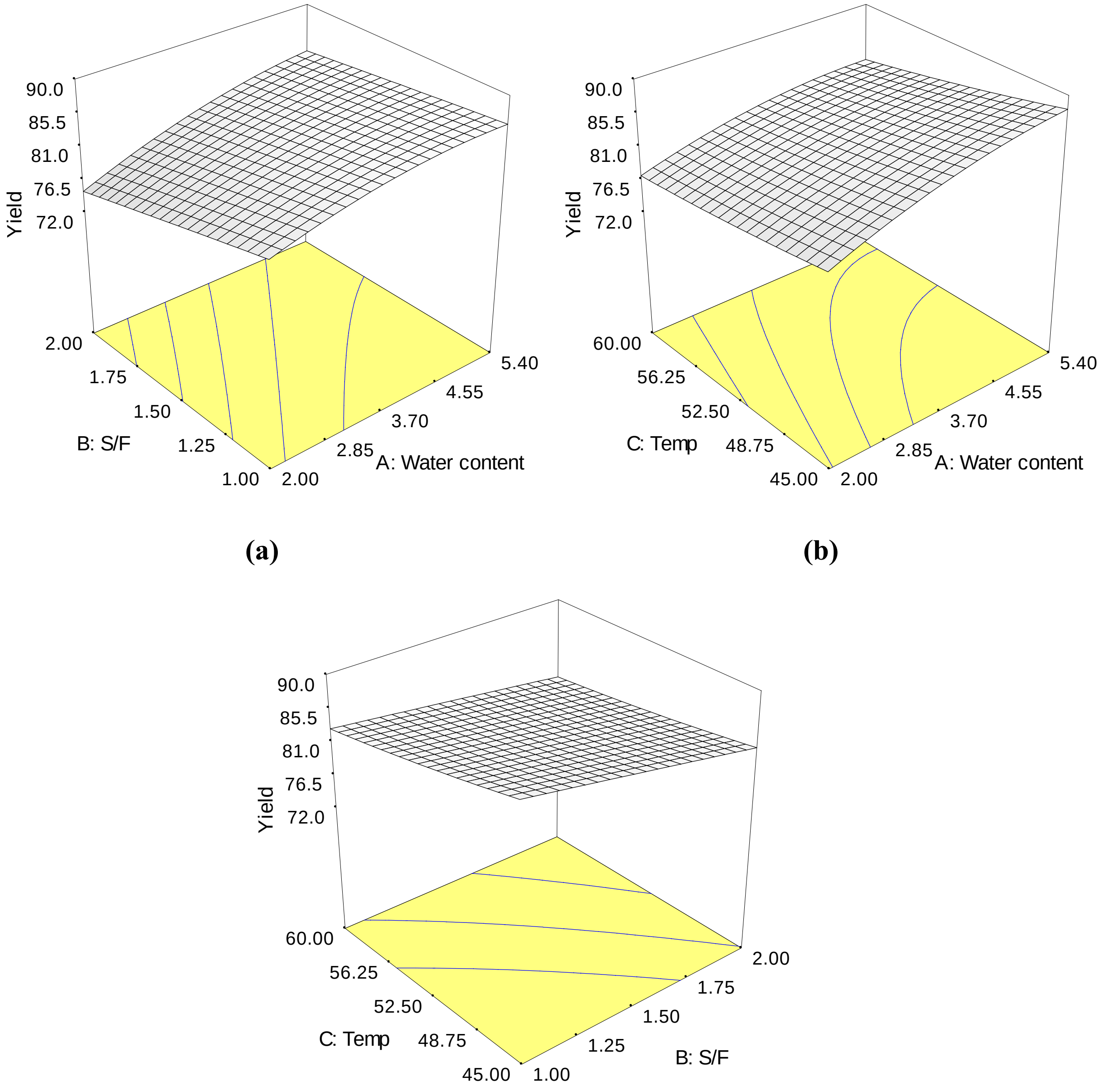
3D surface plots of ESRGO yield (Y_1) versus W_c, S/F, T_E parameters are shown in Figure 4.10a, 4.10b and 4.10c. Figure 4.10a shows that Y_1 increases with an increase in water content (W_c) in solvent and decrease in S/F ratio (S/F) at given T_E. Capacity of solvent (DMF) decreased with addition of water and results in lower dissolution of hydrocarbon molecules in solvent. Higher S/F ratio implies that more molecules of solvent are available to contact the given number of gas oil molecules and leads more interaction among solvent and oil molecules. This results in lowering of the yield of ESRGO. Y_1 is more sensitive to W_c than S/F parameter. This implies that W_c is preferred parameter to change for manipulating the Y_1. It is observed that slope of change in Y_1 is decreasing with an increase in W_c in solvent at any given value of S/F. Y_1 changes linearly with increasing the S/F at any value of W_c. Moreover, the increase in Y_1 is nonlinear with decrease in S/F and increase in W_c. Change in Y_1 is marginal when W_c is increased from 4.55 to 5.40.

It is clear from Figure 4.10b that Y_1 decreases as T_E is increased for any value of W_c. Increase in temperature leads to the increase in capacity of solvent. This leads to more hydrocarbon molecules of gas oil dissolution in solvent. As a result, amount of raffinate (ESRGO) decreases and amount of extract increases. Decrease in Y_1 with an increase in T_E is almost linear at any value of W_c. Further, it is noticed that decrease in Y_1 with increase in W_c is nonlinear and slope of nonlinearity decreases with increased value of W_c at all the value of T_E. Thus, change in Y_1 with respect to T_E is increased with an increase in W_c.

Figure 4.10c indicates that Y_1 decreases as S/F increases for all value of T_E; and Y_1 increases as T_E decreases for all value of S/F. Increase in value of Y_1 when T_E is decreased from 60°C to 45°C at S/F value of 2 is approximately same as S/F is decreased from 2.0 to 1.0 at the T_E value of 60°C. Further, change in value of Y_1 with respect to decrease in T_E from 60°C to 45°C is increased with decreased S/F.

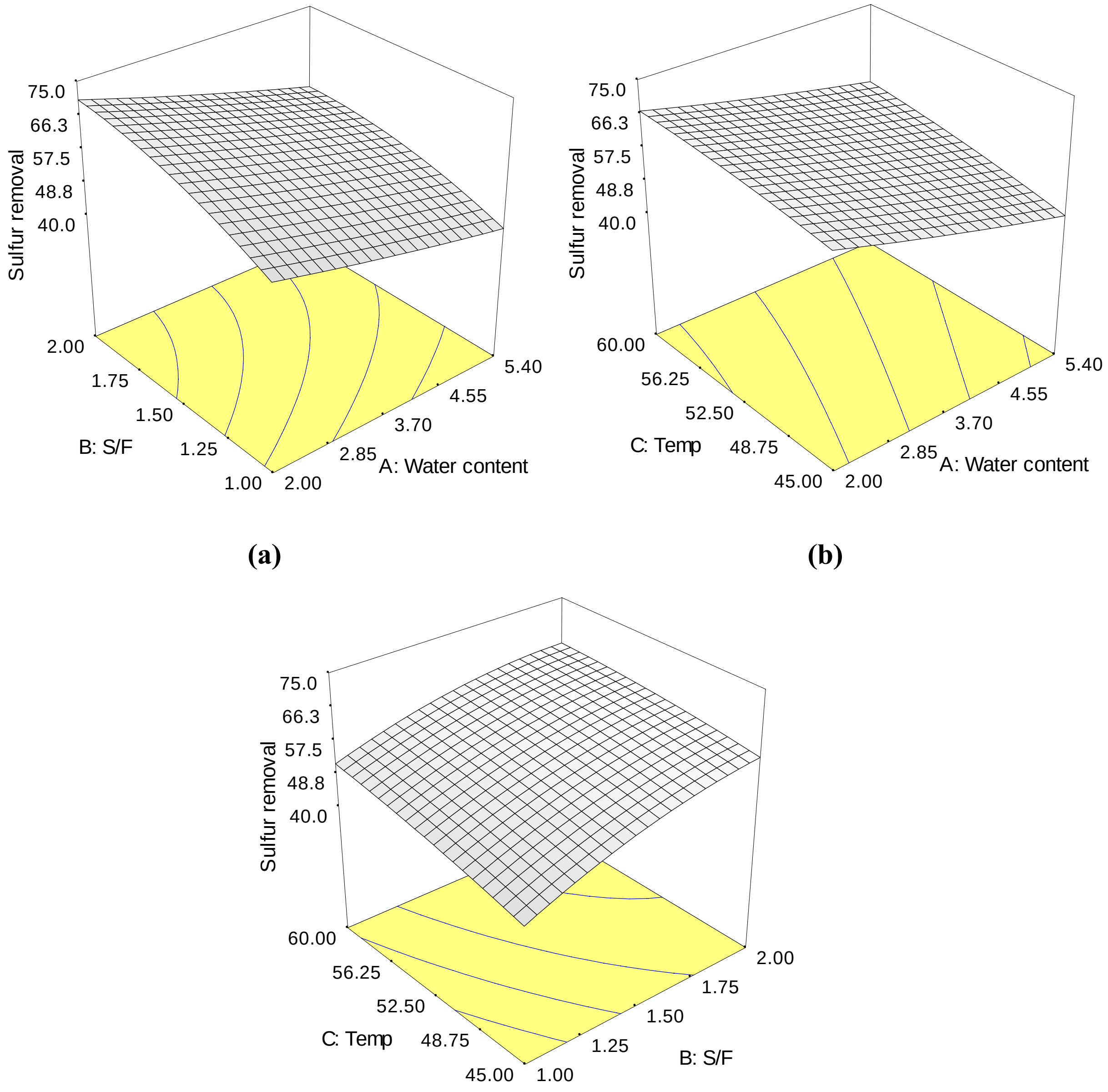
4.4.3.3. Effect of W_c, S/F, T_E on Y_2

Effect of operating parameters, W_c, S/F and T_E, on sulfur removal (response Y_2) is shown in Figure 4.11a, 4.11b and 4.11c. Response Y_2 decreased with an increase in W_c and decrease in S/F ratio (Figure 4.11a). Increased value of W_c in solvent decreases the capacity of solvent to dissolve the hydrocarbon molecules due to its highly polar nature. Therefore, solubility of sulfur compounds decreases in solvent and leads to lower sulfur removal. Further, it is understood that solubility of any hydrocarbon compound in solvent increased with increase in temperature.



(a) (b) (c)

Figure 4.10. Three-dimensional response surface graphs for the desulfurization of SRGO with DMF (a) ESRGO yield (%), Y_1 versus W_c and S/F; (b) ESRGO yield (%), Y_1 versus W_c and T_E; (c) ESRGO yield (%), Y_1 versus S/F and T_E.



(a) **(b)**

(c)

Figure 4.11. Three- dimensional response surface graphs for the desulfurization of SRGO with DMF (a) sulfur removal (%), Y_2 versus W_c and S/F; (b) sulfur removal (%), Y_2 versus W_c and T_E; (c) sulfur removal (%), Y_2 versus S/F and T_E.

In the present study, higher sulfur removal was observed at higher temperature for any value of W_c (Figure 4.11b). Sulfur removal (Y_2) decreased linearly with increase in W_c for any value of S/F whereas Y_2 increased linearly when S/F was increased from 1 to 1.5, however, the linear behavior changed to polynomial curve with decreased slope as S/F increased beyond 1.5.

It is clear from Figure 4.11b that Y_2 increased with decrease in W_c for all value of T_E and with an increase in T_E for any value of W_c. This implies that both parameters affect the response Y_2 in contradictory directions. Increase in Y_1 is linear with increase in W_c at any value of T_E. Sensitivity of Y_2 with respect to T_E is significantly higher at higher value of W_c.

It is understandable that Y_2 increased with an increase in S/F and T_E (Figure 4.11c). Response Y_2 increases linearly with an increase in T_E for all value of S/F. S/F parameter does not affect the response Y_2 in linear fashion for all value of T_E. Y_2 increases linearly till the S/F is increased from 1.0 to 1.6 and afterwards the slop decreases significantly for any value of T_E. Y_2 sensitivity with respect to temperature decreased with increase in S/F whereas sensitivity with respect to T_E is same for all value of S/F.

4.4.3.4. Optimization analysis

Extraction process separates the sulfur compounds from the SRGO using the difference in solubility of sulfur and non-sulfur compounds in solvent. It is inherent in extraction process that solvent not only dissolves the sulfur compounds but also dissolves the non-sulfur compounds. Amount of non-sulfur compounds along with extracted sulfur compounds depend upon the selectivity of solvents for these compounds. It is important to note that higher selectivity of solvent leads to lower loss of non-sulfur compounds. However in highly selective solvent, solubility of sulfur compounds will be lower and this will result in lesser sulfur removal from SRGO. Further, the extent of solubility of SRGO compounds in solvent and its selectivity can be adjusted by adding the anti-solvent (water) in solvent and changing the operating parameters (S/F and T_E). From process economic point of view, it is desirable to obtain the maximum yield of ESRGO with maximum removal of sulfur. However, in extraction process there is a trade-off between the D_{sr} and yield of ESRGO. Thus, the operating conditions and requirement of water content in solvent are not same to maximize both yield of ESRGO (Y_1) and sulfur removal (Y_2).

In present study, the desirability function approach was used to maximize the Y_1 and Y_2 simultaneously. According to Derringer and Suich (1980) the value of the constant, r is specified by the user. For Y_1 and Y_2, value of r=1 and importance = ++ were used during the optimization. The constraints used for lower (L) and upper (U) limit of operating parameters namely W_c, S/F and T_E were: 0.84 (L) - 5.4 (U), 0.80 (L) - 2.34 (U), and 40.0 (L) - 65 (U), respectively.

For Y_1 and Y_2, the minimum acceptable values considered were 70% and 40% and maximum values were 95% and 90% (the maximum value that is feasible), respectively. Equation 4.14 and 4.15 show the desirability of the individual corresponding responses of Y_1 and Y_2 (Kushwaha et al., 2013).

$$d_1 = \begin{cases} 0 & \text{if } Y_1 \le 70 \\ \left(\dfrac{Y_1 - 70}{95 - 70}\right) & \text{if } 70 < Y_1 < 95 \\ 1 & \text{if } Y_1 \ge 95 \end{cases} \tag{4.14}$$

$$d_2 = \begin{cases} 0 & \text{if } Y_2 \le 40 \\ \left(\dfrac{Y_2 - 40}{90 - 40}\right) & \text{if } 40 < Y_2 < 90 \\ 1 & \text{if } Y_2 \ge 90 \end{cases} \tag{4.15}$$

Thus, overall desirability D was calculated by the following equation:

$$D=(d_1 d_2)^{1/2} \tag{4.16}$$

This D value was used as new response by regression analysis. The optimum values of selected variables were: W_c=2.91 (vol.%), S/F ratio=1.70 and T_E=46°C. These values produced maximum D value of 0.438. Correspondingly, yield of ESRGO and D_{sr} were 81.67 and 60.53%, respectively.

4.4.3.5 Analysis of goal importance on optimization

In extractive desulfurization of SRGO, maximum yield (Y_1) of ESRGO and maximum removal of sulfur (Y_2) are desired from process economics point of view. Higher value of Y_1 implies the lower loss of valuable ESRGO with extract and thus improves the process economics. High D_{sr} in extraction will help more in debottlenecking and reducing the operating cost of secondary process to be used for bringing the sulfur in the range of 10-50 ppm. Thus, extent of sulfur removal from SRGO would be governed by the requirements of secondary process. For example, higher sulfur removal in extraction can facilities the hydrotreating operation at lesser sever operating conditions. This will also result in debotelnecking of hydrotreating and hydrogen generation plants. However, lower yield of

ESRGO due to higher removal of sulfur will lead to loss of valuable product with extract. Henceforth, the importance of the response Y_1 and Y_2 would be dependent on secondary process operational requirement and overall operational cost and products sale value. A detailed study of integrated process is required to select the due importance for Y_1 and Y_2. Therefore, it may not be very judicious at this point of time to estimate only one set of optimized operating parameter corresponding to the desirability. Therefore, importance for Y_1 and Y_2 were varied to estimate the optimized values of operating parameters using the maximum desirability approach to understand the effect of goal importance on values of operating parameters. Results are given in Table 4.9. It was observed that W_c and T_E parameters were changed appreciably corresponding to the change in selected importance to the individual goal, Y_1 and Y_2. The value of S/F parameter does not change notably.

Table 4.9. Optimized values of operating parameters, corresponding to the selected goal importance for Y_1 and Y_2.

Goal importance		Optimized Parameter			Y1	Y2	Desirability
Y1	Y2	Water	S/F	Temp			
++	++	2.91	1.70	46.44	81.67	60.53	0.438
+++	++	3.18	1.69	43.27	83.66	56.94	0.451
++++	++	3.33	1.69	41.04	84.98	54.43	0.470
+++++	++	3.48	1.68	40.00	85.91	52.63	0.489
++	+++	2.57	1.71	49.14	79.72	63.86	0.440
++	++++	2.31	1.73	50.55	78.38	65.99	0.449
++	+++++	2.10	1.74	51.38	77.39	67.49	0.461

It implies that the yield of ESRGO to the value of 85.91% with 52.62% sulfur removal can be attained using the optimized parameters when the importance to goal Y_1 and Y_2 are +++++ and ++ respectively, whereas 67.49% sulfur removal with yield of ESRGO 77.39% can be attained when the importance to are ++ and +++++.

4.4.4. Extract Value Addition and Disposal Options

In spite of many advantages of desulfurization of gas oil using solvent extraction, loss of paraffinic compounds with sulfur compounds in extract is considered the drawback of this process. Therefore, it is essential to look the extract disposal options which can add the sufficient value to the extract stream to offset disadvantage of paraffinic material loss. 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 4.12. The concentration of non-aromatics compound which are desirable in ESRGO is decreasing in the extract with decreasing in temperature and increase in W_c in the solvent.

Considering the composition of extract, it should be taken into account that the extract should not be considered as a waste. 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 (Mektta and Cunningham, 1990):

$$BMCI = 473.7S_g - 456.8 + \left(48460/T_b\right) \tag{4.17}$$

where, S_g is liquid specific gravity at 15.5°C 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.

The values of estimated BMCI values along with the estimated S_g of extract streams are tabulated in Table 4.10. Results indicates that BMCI value increases with decrease in T_E and increase in W_c in solvent as selectivity of solvent for aromatic increases with respect to increase in paraffins compound (Figure 4.12). As we know, higher the BMCI, better is 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 W_c 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 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 (, CBFS specification- Indian Oil Corporation limited (http://www.iocl.com/Products/CarbonBlackFeedStockSpecifications.pdf); CBFS specification- Reliance India Limited, (http://www.ril.com/downloads/pdf/carbonstocksspecification.pdf). Fluid catalytic cracker unit (FCCU), delayed coking unit

(DCU), and hydrocracker unit (HCU) are secondary conversion processes used in refinery to covert the heavy fractions of crude into light and middle distillates. Extract obtained in extraction can be routed to these units to produce light and middle distillates and thus value addition to extract. Routing of extract stream containing negligible amount of metal to FCC and hydrocracker catalyst extract will facilities the lower deactivation of catalysts.

Table 4.10. 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 (gm/cm^3)	0.9162	0.9375	0.9396	0.9810	0.9853
Density@15.5° C(gm/cm^3)	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

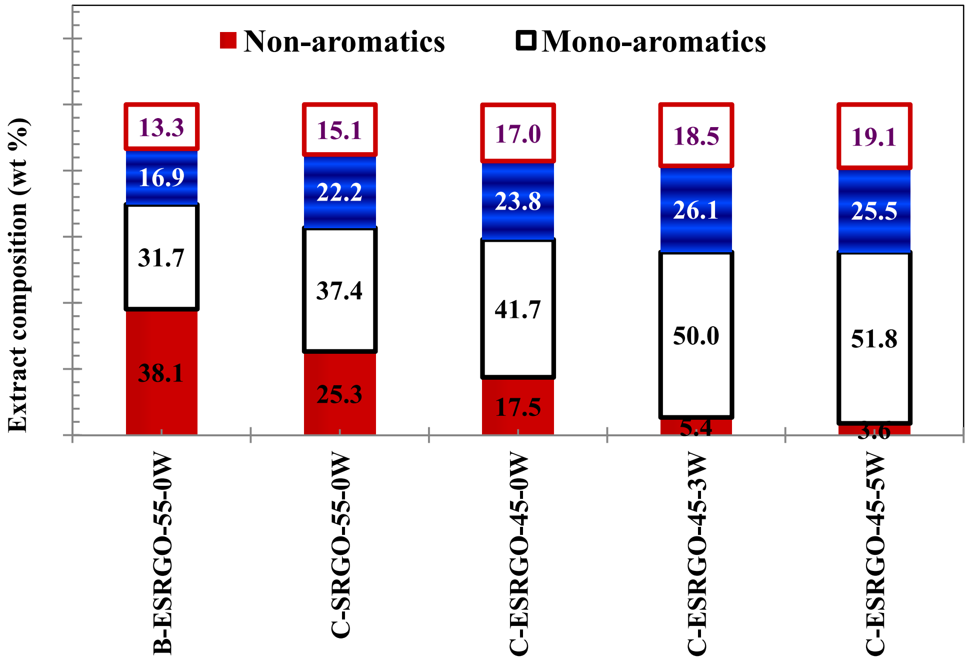


Figure 4.12. Composition of extract phase obtained during batch and continuous extraction using DMF as solvent at various experimental conditions.

Further, conradson carbon residue (CCR) and viscosity of extract stream would be significantly lower 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 (HPI, 2001).

Vacuum gas oil which contains refractive sulfur compounds is processed in hydrocracker to produce the middle distillate. The distillates obtained from hydrocracker are almost sulfur free because it is operated at sever operating conditions of temperature, pressure and hydrogen to oil ratio. In view of this, extract blending with the hydrocracker feed stock seems very attractive for its desulfurization without using sever operating conditions in hydrotreator which would process ESRGO. Considering the significant yield of ESRGO (75 to 90%) on SRGO basis, this approach may reduce the operating and revamp cost of hydrotreating unit significantly at the cost of marginal increase in the operating cost of hydrocracker.

Bio-desulfurization (BDS) process removes sulfur from highly refractive organosulfur compounds which are extremely difficult to be removed by the hydrotreating method. The process conditions used in BDS are mild and do not require hydrogen. This leads to high energy savings in the refinery and significant reductions in greenhouse gas emissions (Mohebali and Andrew, 2008). However, lower reaction rate, large rector volume, huge energy and resource requirement for separation and disposal of water, etc. are the various challenges in commercialization of BDS process (Linguist and Pacheco, 1999; Yu et al., 2006). However, in the amount of extract obtained after extractive desulfurization is generally 10-20% of SRGO. This implies that there is a significant reduction in volume in comparison to SRGO by a factor of 5 to 9. The reduced volume of extract will facilitate the reduction in size of bioreactor, water/oil volume ratio requirement by a factor 5 to 9 if BDS is after extractive desulfurization in comparison to direct SRGO BDS. Therefore, the capital cost required for building the bioreactor and operating cost for separation and disposal of water thus will decrease significantly. Thus, BDS may be attractive for further removal of sulfur from the extracts after extractive desulfurization of SRGO.

Chapter – 5

DESULFURIZATION OF VARIOUS GAS OIL

5.1. GENERAL

Desulfurization process can be made more economical by using combination of processes. It is shown in chapter 4 that selective solvent extraction process can remove the refractive sulfur compounds, polyaromatics and nitrogen compounds to a large extent. Solvent extraction seems to be one of the best options for generating cleaner feed for hydrotreating unit either by eliminating or by drastically reducing the investment and operation cost required for generating the ultra clean gas oil. The solubility of different hydrocarbons of gas oil in a polar solvent generally follows the order: aromatics > naphthenes > paraffins. This is attributed to their molecular structure. It is important to note that gas oil consists of various sulfur compounds such as long chain mercaptans, alkylated thiophene, benzothiophene (BT), dibenzothiophene (DBT), and alkylated BT and DBT. These sulfur compounds have significantly different molecular structure because of which they have different polarity and solubility in a given solvent. Therefore, it is expected that degree of sulfur removal (D_{sr}) from the gas oil will greatly depend on the nature/type of sulfur compounds present in the gas oil. Further, removal of sulfur compound from gas oil in the extraction process will depend on their relative interaction with non sulfur compounds (carrier phase) which itself is governed by composition of carrier phase for a given solvent. Therefore, removal of sulfur compounds from gas oil using solvent will also significantly depend upon the composition of gas oil.

In the refinery, various streams such as straight run gas oil (SRGO), light cycle oil (LCO), coker gas oil (CGO), visbreaker gas oil (VbGO), hydrocracker gas oil (HCGO) are generated in several processes. These streams are blended for generating the gas oil pool. A simplified schematic for gas oil pool generation in refinery is given in chapter 1. Gas oil streams generated from crude, catalytic and thermal cracking of heavy feed have significant different composition in term of paraffinic, aromatics and refractive sulfur compounds concentration. Therefore, operating parameters and solvent system to be used in solvent extraction for sulfur and aromatic removal from LCO, CGO, SRGO and their mixture termed as mixed gas oil (MGO) will be sufficiently different.

This chapter present results of two different types of studies. First part of the study aimed to illustrate the quantitative effect of molecular structure of sulfur compounds and carrier phase composition on their removal from synthetic gas oil mixture and effect of actual gas oil composition on degree of sulfur removal (D_{sr}) and yield of raffinate (Y). To meet these objectives, first, selective solvent extraction of various sulfur compounds from synthetic carrier phases (CP-I and CP-II) and actual gas oil such as SRGO, LCO, CGO and MGOs was carried out using N,N dimethylformamide (DMF) as solvent

In second part, extraction of SRGO, LCO, CGO and MGO using N-Methyl-2-pyrrolidone (NMP) as solvent was carried out to understand the effect of operating variables such as solvent to feed ratio (S/F), extraction temperature (T_E) and water concentration (W_c) in main solvent and composition of real gas oils on important parameters used for evaluation of performance of a solvent extraction processes such as D_{sr}, Y, distribution coefficient (K_s), extraction factor (ε_s) and performance factor ($P_{f,\alpha}$). Further studies were carried out for MGO in single stage and continuous counter current packed bed extractor using the estimated values of T_e, S/F, and W_c by summation of multiplication of volumetric composition of MGO and optimized operating conditions for individual SRGO, LCO and CGO streams. The major issues associated with solvent extraction for gas oil desulfurization are to minimize the loss of valuable hydrocarbon with extract and value addition to extract hydrocarbon. Both these issues have been addressed in the present study by generating pseudo raffinate from the extract phase using water as anti-solvent. Quantitative estimation of distillate products generated from processing the pseudo raffinate in hydrocracker and FCC processes was done so as demonstrate utilization of pseudo raffinate in existing facilities. Strategy for disposal of extract hydrocarbon has been also discussed.

5.2. EXPERIMENTAL

5.2.1. Materials

DMF (99.5+, MERCK), NMP (Min assay 99.7) were used as extraction solvents. Dodecane (99%, SIGMA chemical company), hexadecane (99%+ MERCK), 1-methylnaphthalene (97%, Fluka Chemika), butyl benzene (99%+-Aldrich) were used to prepare the model diesel with model sulfur compounds. Benzothiophene (98% min-HIMEDIA), 3-methyl benzothiophene (96%-SigmaAldrich), dibenzothiophene (99%, ACROS Organic), 4-methyl-dibenzothiophene (95%, ACROS Organic) and 4,6 dimethyl dibenzothiophene (95%, ACROS Organic) were used as model sulfur compounds to prepare model gas oil. All compounds mentioned above were used without any pretreatment. SRGO, LCO and CGO samples were obtained from an Indian refinery. Properties of these actual gas oil samples and mixed gas oil samples (MGO-I, II and III) prepared by mixing of SRGO, LCO and CGO in different proportion are given in Table 5.1. PFPD spectra of SRGO, LCO and CGO are given in Figure 5.1. Anhydrous calcium chloride was used to remove water from hydrocarbon phase.

5.2.2. 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 prepared model gas oils were estimated by X-ray fluorescence (XRF) method by using ASOMA ED XRF analyzer (Spectro Phoenix II make)**.** American standard testing method (ASTM) D86 was used for determining the boiling range of gas oil samples. Boiling range of SRGO, LCO and CGO is given in Table 5.2. Pulsed flame photometric detector (PFPD) inbuilt GC was used to detect the sulfur type analysis. Ultraviolet (UV) visible spectrophotometric technique was used for estimation of mono-, di-, and poly aromatics content in samples. CCR which provide some indication of the relative coke forming tendency of stream was estimated using the ASTM D 4530–03 method.

5.2.3. Apparatus and Procedure

5.2.3.1. Single stage equilibrium extraction

During an experimental run, a known amount of gas oil and solvent was charged in a jacketed glass mixer settler (experimental set up is given in chapter 4.0) provided with a stirrer. T_E was maintained within ±0.5°C with the help of a thermostatic bath. Charge was stirred for 25 min which was sufficient for the establishment of equilibrium. After mixing, residence time of 20 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 estimation of yield of raffinate. The moisture of the solvent free raffinate was removed using the anhydrous calcium chloride. Thereafter, raffinate was analyzed for its sulfur concentration.

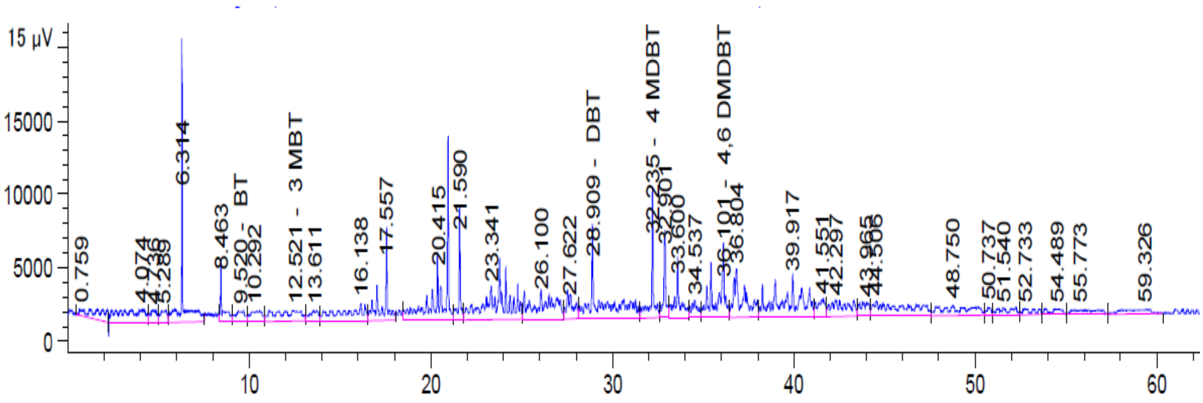
Table 5.1. Properties of SRGO, LCO and CGO feed samples.

Parameter	SRGO	LCO	CGO	MGO-I (50:30:20)	MGO-II (60:25:15)	MGO-III (70:20:10)
Sulfur, (wt.%.)	1.3	0.676	0.268	0.923	1.004	1.072
Density @ 20°C (gm/cm^3)	0.8532	0.9383	0.8529	0.8791	0.8767	0.8732
Mono-aromatics (wt.%)	18.8	17.5	13.5	17.4$^\#$	17.7$^\#$	18.0$^\#$
Diaromatics (wt.%.)	8.2	27.1	11.7	14.9$^\#$	13.8$^\#$	12.6$^\#$
Polyaromatics (wt.%)	6.2	17.9	6.7	10.0$^\#$	9.4$^\#$	8.8$^\#$
Non-aromatics (wt.%)	66.8	37.5	68.1	57.7$^\#$	59.1$^\#$	60.6$^\#$

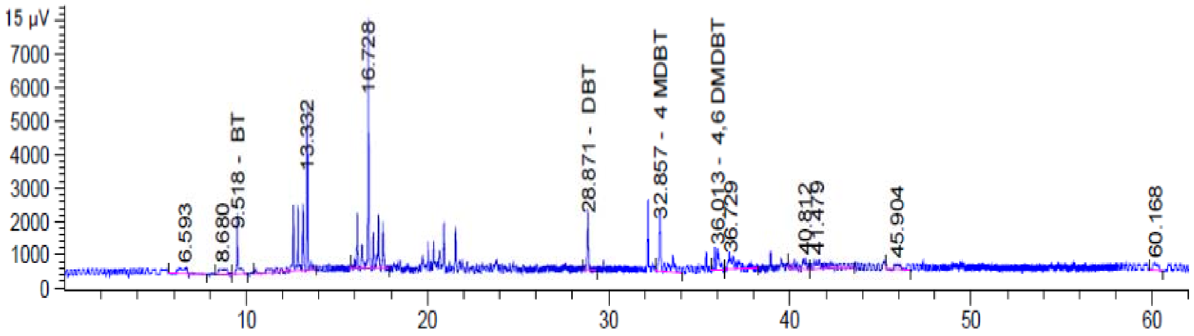
$^\#$ Estimated

Table 5.2. Boiling range (ASTM D86,°C) of SRGO, LCO and CGO feed samples.

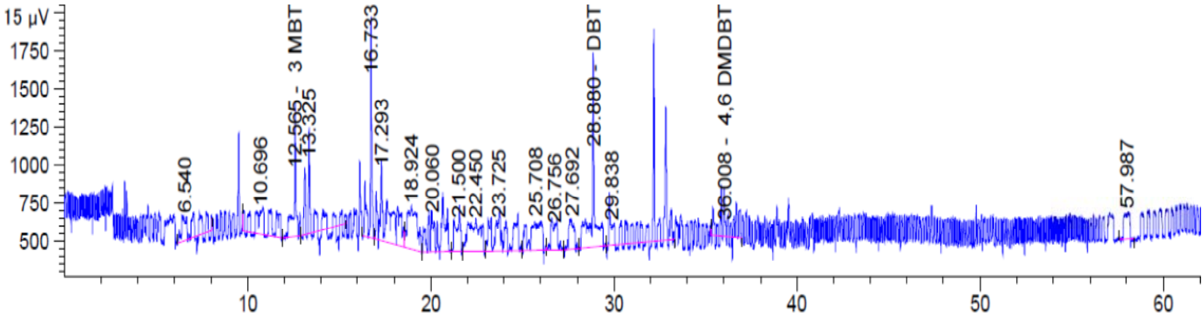
	Boiling point (°C)		
Volume (%)	SRGO	LCO	CGO
Initial boiling point (IBP)	236.5	191.3	169
30 volume%	285.2	282.2	220.3
50 volume%	305.1	308.2	261.1
70 volume%	330.3	335.6	291.5
95 volume%	383.5	376.9	343.1
Final boiling point (FBP)	386.7	382.2	348.3
Distillate	97.7	98	97.8
Residue	1.9	1.8	1.7
Loss	0.4	0.2	0.5



(a) SRGO



(b) LCO



(c) CGO

Figure 5.1. PFPD spectra of SRGO, LCO and CGO.

5.2.3.2. Continuous extraction in packed bed extractor

Continuous counter-current extraction of feed oil was carried out in a jacketed pyrex glass column of 20 mm internal diameter (experimental set up is given in chapter 4). Column was filled up to 140 mm of its height with ceramic intalox saddle packing of 7-9 mm size. Settling zones of 16 mm height were provided on both side of the packing zone at the top and bottom of the column. Feed and solvent were pumped using the metering pumps at the bottom and top of the column, respectively. Flow rates of 5 and 7 ml/min for feed and solvent, respectively, were fixed so as to get the desired solvent-to-feed ratio of 1.4. In extraction runs, feed was used as dispersed phase, the interface was observed at the top of the column. Level of interface was kept constant in the settling zone at the top of the column during the run. Temperature of column was maintained by circulating the hot water in jacket of the column. 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. Raffinate phase and solvent rich were obtained from top and bottom of the column, respectively. Raffinate phase was further treated in the same way as in single stage equilibrium experiments.

5.2.4. Generation of Pseudo Raffinate and Extract Hydrocarbon

Pseudo raffinate is the hydrocarbon rich phase generated by addition of water in extract phase obtained from continuous extraction column. Since, amount of solvent and hydrocarbon in raffinate phase are known, the amount of solvent and hydrocarbon in extract phase can be estimated using the material balance. Amount of water to maintain the given percent of water in solvent of extract phase was estimated. 500 ml of extract phase along with estimated amount of water for corresponding water percent in solvent was retained in batch single stage equilibrium extraction system for 15 min at 40°C. Mixture was stirred for 5 min. Settling time of 45 min was provided for the phase separation. Pseudo raffinate was collected and water washed. Traces of water from pseudo raffinate were removed by using the anhydrous $CaCl_2$. Hydrocarbon phase from the extract phase was generated by adding the excess amount of water and hexane in extract phase in three liter separating funnel. After separation of hydrocarbon phase, the remaining extract phase was treated four times in the same way as described above to remove the hydrocarbon from solvent. Finally, hexane from collected hydrocarbon phase was recovered using the distillation to generate extract hydrocarbon.

5.2.5. Extraction Performance Evaluation Parameters

Dgree of sulfur removal (D_{sr}), yield of desulfurized gas oil (Y) and performance factor ($P_{f,\alpha}$) were used for performance evalaution. The definitions of these parameters are given in chapter 4. Material and component balance equations which were used to estimate the unknown value of aromatics in mixed feed are defined as:

$$F_M = \sum_{ms}^{n} F_{ms} \tag{5.1}$$

$$v_{ms} = F_{ms} / \sum_{ms}^{n} F_{ms} \tag{5.2}$$

$$x_{m,i} = \sum_{ms}^{n} x_{ms,i} v_{ms} \tag{5.3}$$

where, F is mass of feed, raffinate and extract, respectively. Subscripts, M denotes mixture, ms denotes the mixing stream, n denotes number of mixing streams (SRGO, LCO, CGO). v_{ms} denotes fraction of stream, and x_i denotes mass concentration of component, i.

5.3 RESULTS AND DISCUSSION

5.3.1. Effect of Sulfur Type and Carrier Phase on desulfurization

5.3.1.1. Extraction of model sulfur compounds from synthetic carrier phases

Actual gas oil consists of various sulfur compounds such as long chain mercaptans, alkylated thiophene, BT, DBT and alkylated BT and DBT (Song et al., 2006b). Actual gas oil as used in chapter 4 comprised of 66.8% paraffins, 18.8% monaromatics and 14.4 wt.%. polyaromatics. In solvent extraction, impurities get distributed in the solvent and hydrocarbon rich phases. Thus, extractive desulfurization works on the principle of relative solubility of sulfur compound in the solvent and its carrier phase. In the present study, solvent extraction of model sulfur compounds from carrier phase I (CP-I) comprising of dodecane, butyl benzene, methyl naphthalene in the ratio of 66.8, 18.8 and 14.4 wt.%., respectively, (representing the paraffins, monaromatics and polyaromatics compounds) was carried out using DMF as solvent in a jacketed glass mixer settler at S/F=1.0 as per procedure described in the section 5.2.4.1. The results of solvent extraction of these sulfur compounds from CP-I are given in Table 5.3. Results (Table 5.3) clearly indicate that extractability of sulfur compound from other hydrocarbon compounds present in the carrier phase strongly depends on its molecular structure. Sulfur removal for these model compounds followed the order: BT

≈ DBT > 4 methyl-DBT > 3- methyl BT ≈ 4, 6-dimethyl-DBT > 2-N-cctylthiophene >> 1-dodecanethiol. Removal for aromatic sulfur compounds is much higher than non-aromatic sulfur compounds in solvent extraction. This may be attributed to the fact that aprotic solvent (DMF) forms fairly stable Π complex with aromatic sulfur compounds (Gaile et al., 2010). It can be seen from the molecular structure of sulfur compounds and sulfur removal results that D_{sr} decreased with an increase in the number of alkylated group attached with the benzothiophene and dibenzothiophene rings.

However, representing the carrier phase by the single compound for sulfur removal studies is a common practice as reported in the literature to facilitate easier composition analysis (Caero et al., 2005; Xu et al., 2009; Varma et al., 2011). In view of this, solvent extraction of model sulfur compounds from carrier phase (CP-II) represented by hexadecane having boiling point roughly near to the mid boiling point of gas oil was also carried out to understand the effect of carrier phase composition on the degree of various model sulfur compounds removal. D_{sr} for various model sulfur compound from CP-I and CP-II is given in Figure 5.2. It can be seen from the Figure 5.2 that D_{sr} for all sulfur compounds studied is significantly higher for CP-II than CP-I.

Table 5.3. Extraction of model sulfur compounds using DMF as solvent.

Sulfur compound	**Feed (CP1) SC (ppmw)**	**Raffinate SC (ppmw)**	**D_{sr} (%)**
1-Dodecanethiol	852	746	12.44
2-N-Octylthiophene	1122	814	27.45
Benzothiophene	733.4	217.5	70.34
3- Methyl benzothiophene	721.8	277	61.62
Di-benzothiophene	713.4	215.2	69.83
4-Methyl-dibenzothiphene	845.4	298.9	64.64
4,6-Di-benzothiophene	706.4	270.7	61.68

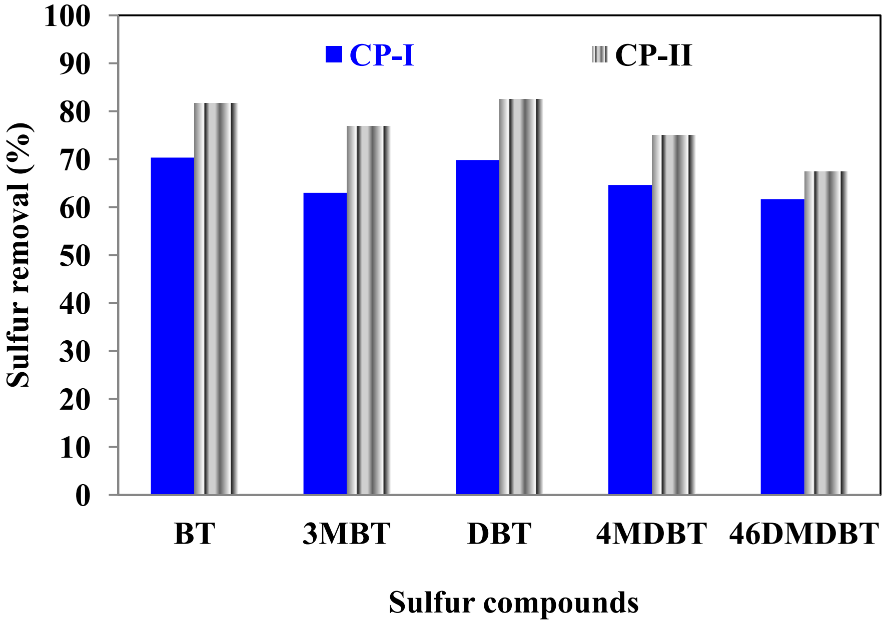


Figure 5.2. Effect of nature of sulfur compounds and carrier phase composition on sulfur removal.

This trend may be attributed to significant different solubility of the carrier phase compounds (CP-I= dodecane, butyl benzene, and methylnaphthalene=66.8: 18.8: 14.4; CP-II= hexadecane) in solvent and their different interactions with sulfur compounds. Lower solubility of hexadecane in polar solvent implies its weaker interaction with solvent molecules whereas higher solubility of butyl benzene and methylnaphthalene indicates stronger interaction with solvent molecules. Therefore, higher removal of sulfur from CP-II implies the weaker interaction of sulfur compound with the carrier phase compound and stronger interaction with solvent molecules. Butyl benzene and methyl naphthalene present in CP-I have much higher solubility in DMF than hexadecane of CP-II. This results in stronger interaction of sulfur compounds with CP-I compounds than CP-II and resulting in lower sulfur removal from CP-I than CP-II.

5.3.1.2 Extraction of actual gas oil using DMF as solvent

In view of the solubility based operational principle of solvent extraction, it will be very interesting to see that how the composition of various actual gas oil streams generated in the refinery affect the solvent extraction process. The solvent extraction of SRGO, LCO, CGO and mixed gas oil samples ((MGO-I, II and III) was carried out using the DMF solvent at S/F of 1.0. Properties and volume of desulfurized gas oil (raffinate) samples were measured. Measured properties and estimated responses are given in Table 5.4.

It is clear from Table 5.1 that the composition of SRGO, LCO and SRGO in term of nonaromatic, mono, di- and poly-aromatics is quite different. Results (Table 5.4) clearly indicate that sulfur removal and raffinate yield using solvent extraction strongly depends upon different component concentration in the feed. D_{sr} followed the order: CGO > LCO > SRGO. This trend is similar to total sulfur content in these gas oil streams. It is quite possible that LCO and CGO generated from catalytic and thermal cracking of heavy feed stocks have the aromatic sulfur compounds with smaller alkylation chain in comparison to the SRGO. These gas oils may also contain some nonaromatic sulfur. Extractability of sulfur compound decreases with either increase in their alkylation chains or number of alkylation groups (Table 5.3). This may be reason of lowest D_{sr} for SRGO. Though, the nature of sulfur compounds in both LCO and CGO streams would be similar but their drastically different composition (LCO has very high concentration of di- and poly-aromatics than CGO) may be reason for their different D_{sr}.

This may be explained from the fact that during the extraction, part of solvent is utilized in dissolving the aromatics compounds along with sulfur. Thus, effective solvent amount utilized for sulfur compounds removal from LCO is lower than CGO and leads to lower sulfur removal than CGO. Raffinate yield values followed the order: SRGO > CGO >> LCO. It is known that compounds having low solubility in solvent are recovered as raffinate. Order of raffinate yield seems to depend on the amount of total aromatics in the gas oil streams due to their high solubility in solvent.

Table 5.4. Solvent extraction of gas oil streams with DMF solvent at 45°C, S/F: 1.0.

	SRGO	LCO	CGO	MGO-I (50:30:20)	MGO-II (60:25:15)	MGO-III (70:20:10)
Raffinate properties						
Sulfur in Raffinate (%)	0.810	0.304	0.093	0.510	0.571	0.649
Density@20° (gm/ml)	0.8352	0.8795	0.8225	0.8461	0.8451	0.8436
Calculated responses						
Gas oil Yield (%)	81.0	22.40	66.80	69.60	72.40	76.80
Extraction factor	1.02	9.60	3.49	1.70	1.52	1.23
Distribution coefficient	0.64	2.80	6.53	3.56	3.62	3.63
Sulfur removal (%)	37.7	55.1	65.4	44.7	43.1	39.5

For the mixed gas oil (MGO-I, MGO-II and MGO-III obtained by mixing SRGO, LCO and CGO in different ratio), yield value increases and D_{sr} decreases as expected with an increase in percentage of SRGO in MGO. Extraction factor (ε_s) represents the amount of sulfur compounds in the extract phase. ε_s values for the tested gas oil samples are in order: LCO > CGO > MGO-I > MGO-II > MGO-III > SRGO. This trend is just the reverse of that observed for the yield values. Distribution coefficient (K_s) implies the divisional tendency and relative concentration of sulfur compounds in extract and raffinate phase and represents the ease of sulfur removal. K_s values for these gas oil samples are in the order: CGO > LCO > MGO-I ≈ MGO-II ≈ MGO-III > SRGO. K_s value for CGO is ~2.5 fold higher than LCO and ~10 times higher than SRGO. Ks value for LCO is ~4 times higher than SRGO. It is important to note that ε_s and K_s value for LCO and CGO are in reverse order even when it is expected that LCO and CGO both may have similar kind of sulfur compounds. Higher value of K_s for LCO indicates that amount of sulfur extracted in extract phase for one unit sulfur in the LCO feed is more than CGO sample. However, due to high aromatic content of LCO, the concentration of sulfur in LCO extract phase is lower than CGO and resulting in lower K_s value.

Figure 5.3 clearly reveals that the decreasing trend in the yield is similar to increasing trend in aromatic content for gas oil samples (SRGO, LCO, CGO, MGO-I, MGO-II, and MGO-III). However, D_{sr} values do not follow the any trend with respect to aromatic content but follow the trend with respect to sulfur content in these gas oil streams. Further, results given in Table 5.4 indicate that single stage extraction of SRGO, LCO, CGO using DMF solvent can remove the sulfur to the extent of 37.7, 55.1 and 65.4%, respectively. It is shown in chapter 4 that sulfur removal from SRGO in continuous packed bed extraction column is much better than the single stage extraction (single stage=37.7%; packed bed=65%) due to availability of more than one theoretical separation stage and increased concentration gradient between solvent and gas oil phase. This sulfur removal performance will further improve in industrial packed bed extractor which has significant higher height than laboratory scale extractor. It is important to note that D_{sr} for LCO is much higher than SRGO. However, amount of LCO (~77.6%) dissolved in solvent is also drastically higher than SRGO (19%) at the used operating condition of S/F, temperature and without addition of anti-solvent in DMF solvent. For mixed gas oil samples also, the amount of dissolved part of sample in solvent followed the order of percentage of LCO in MGO. This indicates that solvent extraction of LCO using the pure DMF is not economically feasible at these operating conditions.

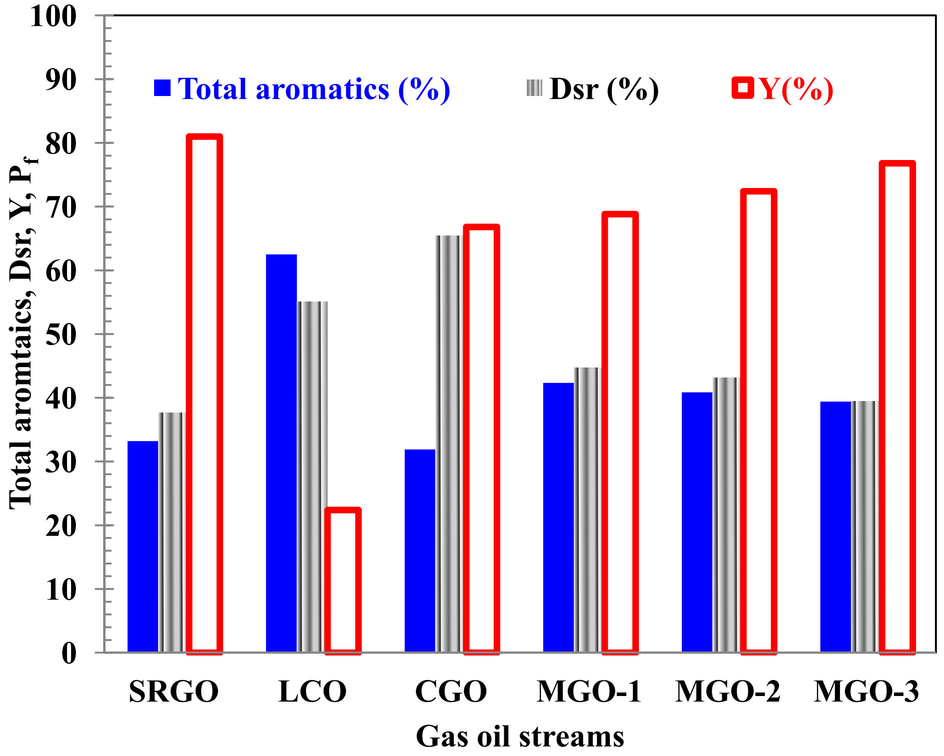


Figure 5.3. Effect of aromatic content on extraction performance parameters.

There is a need to increase the yield of LCO raffinate to a reasonable extent with considerable sulfur removal. It is known that antisolvent reduces the solvency power of solvent which improve the yield of raffinate at the expense of decrease in sulfur removal. Amount of water in solvent is governed by composition of gas oil. Thus, amount of water in DMF will be significantly different for LCO in comparison to SRGO (detail given in chapter 4) to obtain reasonable value of D_{sr} and Y. S/F and T_E would also be different than that optimized for SRGO in chapter 4. This study illustrates the importance of feed composition on need of adjustment of extraction process operating parameters and solvent system for effective sulfur removal from LCO.

5.3.2 Effect of Real Gas Oils Composition on Desulfurization using NMP as solvent

5.3.2.1. Single stage extraction of SRGO, LCO, and CGO

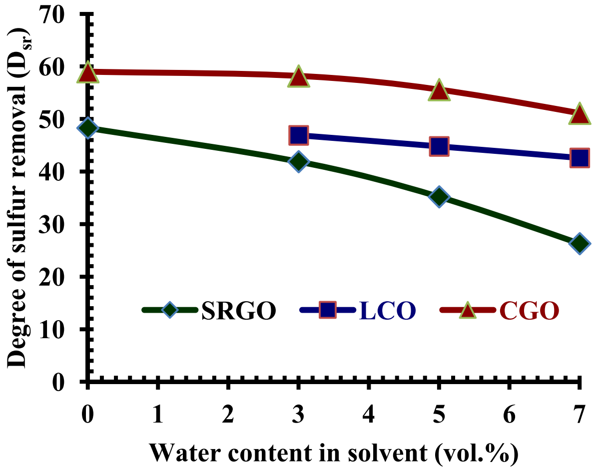
Solvent extraction process works on the principle of solubility difference between solute and carrier phase in solvent. It is apparent that solubility of compounds in solvent during extraction process can be modified to certain extent by modifying the operating conditions such as S/F ratio, T_E and more particularly solvency power of solvent using anti-solvent (water). The results of experiments carried out for studying the effect of these operating parameters on performance of extraction process for each sample gas oil stream are discussed in subsequent sections.

5.3.2.1.1. Effect of water concentration in solvent (W_c): Solvent extraction of actual SRGO, LCO, CGO was carried out using NMP as per procedure described in section 5.2.4.1 at S/F of 1.0 and T_E of 45°C for analyzing the effect of water content in solvent (W_c) on Y, D_{sr} and $P_{f,\alpha}$ which were estimated using correlations described in the section 5.2.6. The properties of raffinate samples generated during the extraction experiments are given in Table 5.5.

It can be seen from the results (Table 5.5) that within the selected range of W_c (0.0-7.0 vol.%) in solvent, both sulfur content in (SC) raffinate and yield (Y) of raffinate increases with an increase in water content of solvent. Y value for these streams followed the order: SRGO > CGO > LCO which is the same order as of nonaromatic content in these samples. It is important to note that increase in Y by addition of first 3.0 vol.% of water in solvent is much higher than the same amount of subsequent water addition. It was observed that LCO does not form two phases with the pure NMP. The most probable reasons for this phenomenon is high solvency power of NMP than other solvents and high concentration of aromatic in LCO which leads to dissolution of huge quantity of hydrocarbon in the solvent and decreases the density difference between extract and raffinate phase and large concentration of aromatics in extract phase does not leave the nonaromatic compounds to form raffinate phase at the operating condition of single stage extraction. Addition of water to NMP decreases its solvency power for hydrocarbons and results in two phase formation. In view of this, application of NMP without water dilution cannot be used for LCO extraction. D_{sr} and $P_{f,\alpha}$ which combine the contradicting effect of water content on sulfur content and for the equal weight factor assigned to Y and D_{sr} are given in Figure 5.4. It is observed that gradient of change in D_{sr} and $P_{f,\alpha}$ with increase in W_c is different for different SRGO, LCO and CGO samples. For selected range of W_c, D_{sr} follows the order: CGO > LCO > SRGO.

Table 5.5. Effect of water content in solvent (W_c) on sulfur content in raffinate and yields of raffinate (Y%) at S/F of 1.0 and T_E of 45°C.

Water Content	Sulfur, wt.%.			Yield, vol.%		
	SRGO	LCO	CGO	SRGO	LCO	CGO
0.0	0.704	S.F.	0.110	80.0	S.F	48.0
3.0	0.790	0.359	0.112	88.8	42.0	68.8
5.0	0.881	0.373	0.119	90.0	48.4	74.0
7.0	1.003	0.388	0.131	93.6	56.0	79.2



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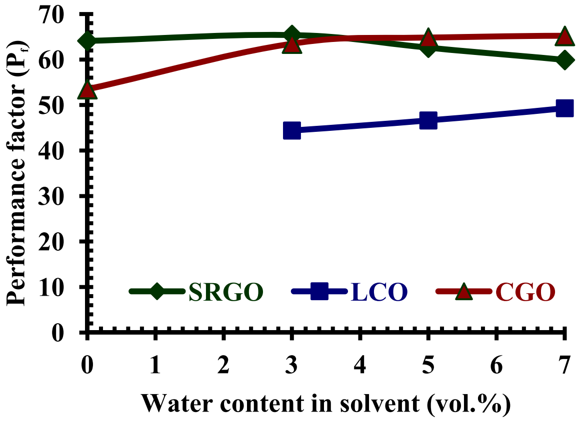


(b)

Figure 5.4. Effect of water content in solvent (W_c) on degree of sulfur removal (D_{sr}) and performance factor ($P_{f,\alpha}$).

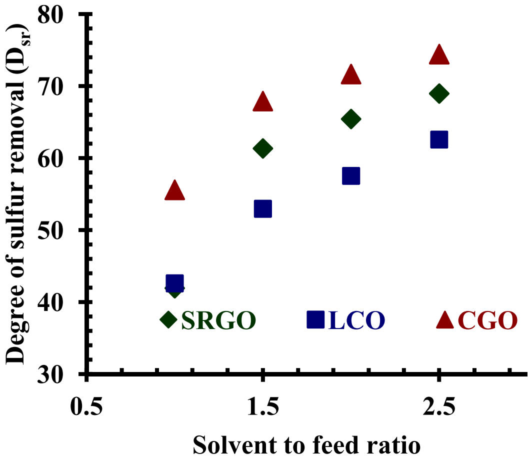
It may be seen that absolute and slope change in D_{sr} is maximum for SRGO and minimum for LCO. $P_{f,0.5}$ values for SRGO first increases and then decreases with an increase in W_c. For LCO stream, $P_{f,0.5}$ continuously increased with an increase in W_c, however, the change in the slope of $P_{f,0.5}$ is very small. For CGO, $P_{f,0.5}$ increases with an increase in W_c, however, change in $P_{f,0.5}$ after 5% value of W_c is marginal. $P_{f,0.5}$ values for SRGO is higher than LCO till the W_c value of 3% beyond that reverse trend is observed. This is attributed to higher SRGO raffinate yield with these W_c superseding the higher D_{sr} of CGO. In view of above, value of W_c values of 3%, 7% and 5% seem to be best for SRGO, LCO and CGO, respectively.

5.3.2.1.2. Effect of solvent to feed ratio (S/F): It is known that higher S/F ratio enhances the extent of removal of impurities from the feed but also results in loss of the desired molecules along with impurity molecules in the solvent. To analyze the effect of S/F for the SRGO, LCO and CGO feeds sample, single stage solvent extraction of these feeds at various S/F ratios was carried out with aqueous NMP containing respective optimized W_c value and at T_E=45°C. Analysis of raffinate samples is given in Table 5.5. As it is expected, S/F is found to affect the sulfur content in raffinate and Y values, and that the sulfur content of raffinate and Y values decreases with an increase in S/F. But percent change in sulfur content and Y is not same for all feed and depends on the feed composition.

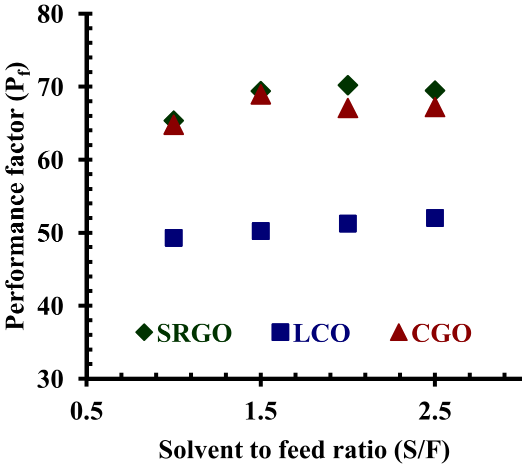
D_{sr} and $P_{f,0.5}$ for SRGO, LCO, and CGO samples are given in Figure 5.5. It is clear that the gradient for change in D_{sr} removal is highest for first 0.5 addition to the base S/F ratio of 1.0. It is observed that at S/F value of 1.0, the D_{sr} of SRGO and LCO are comparable but for S/F ratio higher than 1.0, D_{sr} of SRGO sample is much higher than that of LCO. This may be attributed to the much higher sulfur content of SRGO than LCO and their much different aromatic content. The $P_{f,0.5}$ values for all samples do not show the similar and unidirectional trend with increase in S/F. Change in $P_{f,0.5}$ value for SRGO and LCO streams is marginal after S/F value of 1.5 and 1.0, respectively, whereas $P_{f,0.5}$ values for CGO is maximum at S/F value of 1.5. This change illustrates that after certain value of S/F, the tradeoff between increase in D_{sr} and decrease in Y is established. In solvent extraction process, solvent being an expensive material, it is recovered from extract and raffinate phases for its reuse to sustain the economics of the process. Since for gas oil having the boiling range up to 380°C, small amount of solvent from raffinate phase can be recovered by using the water washing but solvent needs to be vaporized for its recovery from solvent rich extract phase.

Table 5.6. Effect of solvent to feed ratio (S/F) on sulfur content in raffinate and yields of raffinate (Y) at SRGO-W_c=3.0; LCO-W_c=7.0; CGO-W_c=5.0; T_E =45°C.

S/F	Sulfur (wt.%)			Yield (vol.%)		
	SRGO	LCO	CGO	SRGO	LCO	CGO
1.0	0.790	0.388	0.119	88.8	56.0	74.0
1.5	0.526	0.318	0.086	77.5	47.5	70.0
2.0	0.470	0.287	0.076	75.0	45.0	62.5
2.5	0.422	0.253	0.069	70.0	41.5	60.0



(a)



(b)

Figure 5.5. Effect of solvent to feed ratio on degree of sulfur removal (D_{sr}) and performance factor ($P_{f,0.5}$).

In view of latent heat of vaporization requirement, it is easy to understand that solvent recovery is an energy extensive step. The energy requirement will depend on the amount of solvent to be recovered from the extract phase which in turn depends on the S/F used in the process. Considering this, the S/F values of 1.5, 1.0 and 1.5 seem to be best for solvent extraction of SRGO, LCO and CGO, respectively.

5.3.2.1.3. Effect of extraction temperature (T_E): It is reported in literature that was observed in our previous solvent extraction study that T_E value affects the selectivity and solvency power of solvents in solvent (Krishna et al., 1987). Extraction process which basically governs the D_{sr} and Y. For analyzing the effect of T_E on Y, D_{sr}, and $P_{f,\alpha}$, extraction experiments for SRGO, LCO and CGO streams were carried out at 45, 55 and 65°C with selected W_c and S/F values optimized. Results of above experiments are given in Table 5.7. Results suggest that sulfur content in raffinate and Y decrease whereas D_{sr} increases with an increase in T_E. Also, decrease in $P_{f,0.5}$ with increase in T_E is observed. This suggests that rate of decrease in raffinate yield is higher than corresponding increment in D_{sr} with an increase in T_E. It can be understand that on increasing the weight factor (α) to D_{sr}, $P_{f,\alpha}$ value increases. But, raffinate yield (Y) may become important after meeting the given specification of sulfur content in raffinate. Therefore, increase in D_{sr} with increase in T_E will affect the process economic and performance of the process adversely. Therefore, selection of temperature will greatly depend on the demand of the situation.

Table 5.7. Effect of extraction temperature (T_E) on sulfur content in raffinate and yields of raffinate at SRGO: W_c=3.0, S/F=1.5; LCO: W_c=7.0, S/F=1.0; CGO: W_c=5.0, S/F=1.5.

Extraction	**Sulfur (wt.%)**			**Yield (vol.%)**		
Temp.(°C)	SRGO	LCO	CGO	SRGO	LCO	CGO
45	0.526	0.388	0.086	77.5	56.0	70.0
55	0.465	0.378	0.082	71.0	50.0	67.0
65	0.437	0.362	0.084	68.5	42.0	62.5
	Degree of sulfur removal			Performance factor		
45	61.3	42.6	67.9	69.4	49.3	70.2
55	65.8	44.1	69.4	68.4	47.0	68.2
65	67.9	46.4	68.7	68.2	44.2	65.6

5.3.2.2. Single stage and continuous extraction of MGO

In the refinery, gas oil streams from ADU, FCC and delayed coking unit (DCU) are blended to make MGO which is generally hydrotreated to meet the sulfur and aromatic specifications required for its sale in the open market. In general, the MGO contains 60-75% SRGO, 30-15% LCO and 10-20% CGO depending up on the configuration of refinery and type of processed crude. In the present study, MGO was prepared by mixing SRGO, LCO and CGO in the volumetric ratio of 70:20:10. Batch and continuous extraction of MGO was carried out using the values of T_E, S/F, and W_c estimated using the correlation given below:

$$OP_{e,j} = \sum_{i}^{n} v_i OP_{i,j} \tag{5.4}$$

where, $OP_{e,j}$ is the estimated operating parameter for MGO with j being W_c or S/F or T_E; $OP_{i,j}$ and v_i are optimized parameters and volume fraction, respectively, for i=SRGO, LCO and CGO. Analysis of MGO and products obtained from the batch and continuous extraction of MGO are given in Table 5.8 whereas boiling range of MGO, extract and raffinate obtained from the MGO continuous extraction is given in Table 5.9. It can be clearly seen from the results (Table 5.8) that solvent extraction process is capable of removing the refractive sulfur compounds and aromatics compounds to a significant extent. The sulfur and aromatic removal efficiency of a continuous counter current extraction is significantly higher than the batch extraction process. This is attributed to availability of more than one equilibrium stage in continuous extractor and improved concentration gradient between contacting portion of solvent and feed. In the continuous counter current extraction, raffinate phase leaves the extractor at a location where it is in the contact with the solvent having zero impurities whereas in batch extraction, the raffinate phase is in equilibrium with the extract phase having significant impurities to be removed from feed. This results in higher concentration gradient in continuous column than batch extraction. It is clear that sulfur, di-aromatics and poly-aromatics compounds can be removed from the MGO upto the extent of 76.5%, 93.5% and 95.2% using the continuous extraction column. $P_{f,\alpha}$ values of continuous column are higher than batch extraction which reveals the importance of more theoretical separation stage available in continuous extraction.

Table 5.8. Analysis of feed and products obtained from MGO extraction (Feed: SRGO, LCO and CGO volumetric ratio= 70:20:10; S/F=1.4 and T_E=45°C, W_c=4.0%, α=0.5).

Properties of stream	Feed	R- Batch	R- Continuous
Sulfur (wt.%)	1.171	0.512	0.275
Density @ 20° C (gm/ml)	0.8692	0.8386	0.82164
RI at 20° C	1.4872	1.4661	1.4554
Mono-aromatics (wt.%)	14.6$^{(1)}$	10.2	7.2
Di-aromatics (wt.%)	13.9$^{(1)}$	7	0.9
Poly-aromatics (wt.%)	8.3$^{(1)}$	2.8	0.4
Non-aromatics (wt.%)	63.2$^{(1)}$	80	91.5
Calculated response			
Yield%	--	72.1	63.3
Sulfur removal (D_{sr})	--	56.3	76.5
Performance factor ($P_{f,\alpha}$)	--	64.2	69.9
Mono-aromatics removal (%)		30.3	50.8
Di-aromatics removal (%)		49.5	93.5
Poly-aromatics removal (%)		66.2	95.2

$^{(1)}$Estimated values; R= raffinate; E= extract.

Table 5.9. Boiling range of MGO and its raffinate and extract products (ASTM D-86).

Volume%	MGO	R-EPCE	E-EPCE
IBP	201.3	219.4	185.3
30	279.6	286	272.3
50	302.6	307.5	297.1
70	330.6	334.2	328.5
FBP	383.7	385.3	383.6
Distillate	97.7	97.7	97.6
Residue	1.9	1.9	2
Loss	0.4	0.4	0.4

MGO=mixed gas oil; R-EPCE and E-EPCE=raffinate and extract obtained from continuous extraction of MGO, respectively.

The extent of sulfur content in the raffinate will depend upon requirement of end use process for raffinate. Therefore, selection of value of α to evaluate the $P_{f,\alpha}$ may vary depending upon the importance of sulfur content and yield of desulfurized MGO in that situation. Considering this, the sensitivity analysis of $P_{f,\alpha}$ with respect to α value for MGO batch and continuous extraction was estimated and is given in Figure 5.6. The value of $P_{f,\alpha}$ for batch extraction decreases whereas for continuous extraction increases with an increase in α value assigned to the D_{sr}. Reverse trends in $P_{f,\alpha}$ value for batch and continuous extraction are due to the reverse trend of value of Y and D_{sr} values.

5.3.2.3. Generation of pseudo raffinate and extract

In solvent extraction of gas oil, it is desirable to maximize the yield and minimize the sulfur content of desulfurized gas oil. It is known that there is no sharp separation between impurity compounds and desired compounds in the extraction process. There is loss of desired compounds with sulfur and aromatics compounds in extract phase. Even sometimes, loss of desired paraffinic compounds with extract becomes undesirable as their presence deteriorates the quality of extract to be used as carbon black feedstock (CBFS). Therefore, removal of paraffinic rich material from the extract phase obtained from the continuous extraction column will be very useful to produce the hydrocarbons which can be further treated in secondary process to generate the distillate product and to improve the quality of extract to be used as CBFS. Pseudo raffinates and extract hydrocarbon were generated from the extract phases using the procedure described in the section 5.2.5. Pseudo raffinate (PR1) was generated from the extract phase of continuous extraction column by addition of given amount of water corresponding to given W_c (8%) in extract phase solvent. Pseudo raffinate (PR2) was generated from the extract phase after generating the PR1 by further addition of given amount of water to increase its concentration in extract phase solvent to from 8 to 12%. Properties of pseudo raffinates and extracts are given in Table 5.10. Marginal lower value of density and RI values for PR1 and higher value for PR2 in comparison to MGO suggest that PR1 contains marginal lower aromatic content and PR2 contains marginal higher aromatic content than MGO. Yield of combined mixture of PR1and PR2 is 9.82%. Properties of their mixture can be estimated by multiplying their mass in the mixture and property of blending stream. Properties of pseudo raffinate suggest that this is valuable material and can be processed in secondary conversion processes such as hydrocracker and FCC for generating the distillate products with reduced sulfur content. Detail of pseudo raffinate and extract utilization in potential options is discussed in the subsequent section.

5.3.2.3.1. Utilization of pseudo raffinate: Yield of pseudo raffinate varies in the range of 5-15%. It is common practice to design a unit with 15-20% over design margin. Considering this, it is quite possible to process the generated PR in existing hydrocracker and FCC. Hydrocracker and FCC are designed for processing the heavier feed stocks having boiling range up to ~450-550°C and operate at high sever operating conditions. PR1 and PR2 have been generated from the gas oil having the boiling range up to ~380°C. The metal content and viscosity of crude distillate fractions increase with increase in their boiling range.

Metal content of PR1 and PR2 will be much less than the heavy feed stocks used in hydrocracker and FCC, therefore, their blending with conventional feedstock would be helpful in diminishing deactivation of catalyst. The quantitative estimation of distillate products for processing of the PR1 and PR2 in hydrocracker and FCC was carried using the correlations given in the literature (HPI, 2001). Since the PR1 and PR2 are generated from the extract phase obtained from continuous extraction of MGO, their average boiling point will be close to extract hydrocarbon obtained from the extract phase of MGO continuous extraction (EEPCE). Therefore, distillation data of E-EPCE was used to represent the average boiling point of PR1, PR2 and PR-1&2 streams in the correlations used for quantitative estimation of distillate products for processing of the PR1 and PR2 in hydrocracker and FCC**.** The values of products yield generated in hydrocracker and FCC units for PR-1, PR-2 and their mixture PR-1and 2 are given in Table 5.11.

5.3.2.3.2. Utilization of extract: The application of extract as CBFS in carbon blacks generation unit is one of the potential options for its utilization without any further processing. It is known that quality of CBFS is measured in term of its bureau of mines correlation index (BMCI) value. Therefore to evaluate the feasibility of extract utilization as CBFS, BMCI of extract products was estimated using the correlation 4.17 given in chapter 4.

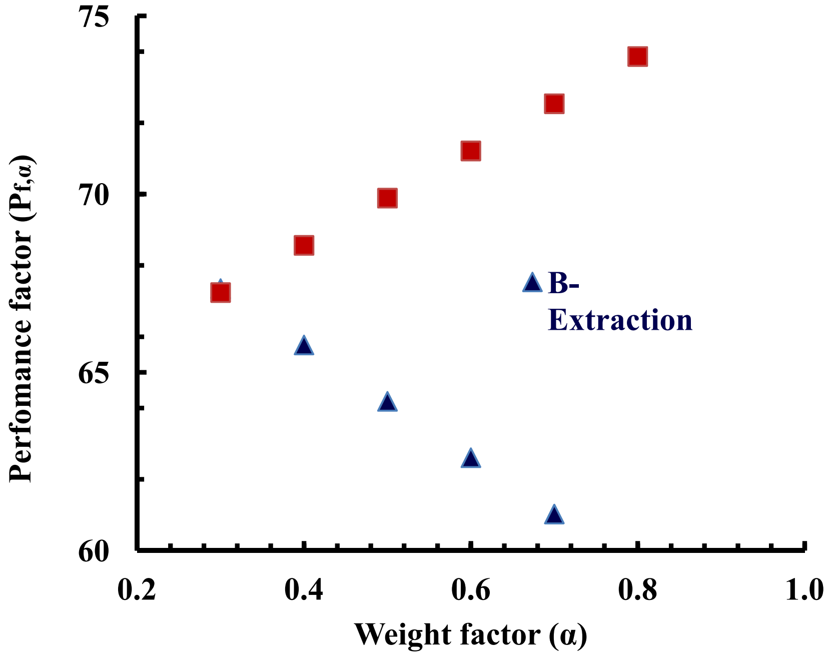


Figure 5.6. Sensitivity analysis of $P_{f,\alpha}$ with respect to α value(B=Batch extraction; C=Continuous extraction).

Table 5.10. Properties of pseudo raffinate and extract samples.

Properties	PR1 (Wc=8.0%)	PR2 (Wc=12.0%)
Pseudo Raffinate		
Sulfur (wt.%)	1.1215	1.5821
Density @ 20° C (gm/cm^3)	0.86147	0.889
RI at 20° C	1.4826	1.4993
Yield on feed basis (vol.%)	5.34	4.48
Extract hydrocarbon		
Properties	E-EPCE	E-EPSRG
Sulfur (wt.%)	2.376	2.531
Density @ 15.5°C (gm/cm^3)	0.95230	0.98144
Specific gravity @ 15.5°C	0.95280	0.98194
Avg. boiling point (°C)	299.3	299.3
BMCI	79.5	93.3
CCR (wt.%)	NT	0.18

E-EPCE= Extract obtained from extract phase of continuous extraction (EPCE); E-EPSRG= Extract obtained from extract phase of pseudo raffinate generation (EPSG); RI= refractive index; BMCI=bureau of mines correlation index; NT= Not tested.

Values of estimated BMCI values along with the estimated S_g of extract samples are tabulated in Table 5.11. It can be seen that BMCI value (Table 5.10) of extract obtained from extract phase of pseudo raffinate generation (E-EPSRG) is significantly higher in comparison to extract obtained from extract phase of continuous extraction (E-EPCE). It suggests that addition of water in extract phase has increased the concentration of aromatic compounds in extract hydrocarbon by concentrating the nonaromatic compounds in pseudo raffinate. This has resulted in drastic improvement in the quality of extract hydrocarbon to be used as CBFS. It may be mentioned that the BMCI values and sulfur content of E-EPSG is in the range for CBFS which are being marketed by refineries in India (CBFS specification, http://www.iocl.com/Products/CarbonBlackFeedStockSpecifications.pdf).

Table 5.11. Products yield distribution for pseudo raffinate processing in hydrocracker and FCC unit.

Hydrocracker unit			
Product name	**PSR-1**	**PSR-2**	**PSR-1&2**
H_2 (wt.%)	2.38	2.96	2.60
H_2S (wt.%)	1.19	1.68	1.42
Light Gasoline (wt.%)	9.38	7.97	8.84
Refinery fuel Gas (wt.%)	1.88	1.75	1.83
C4 LPG (wt.%)	5.53	4.70	5.22
Naphtha (wt.%)	29.08	24.70	27.42
Diesel (wt.%)	55.31	62.16	57.87
Fluidized catalytic cracking unit (FCC)			
Coke (wt.%).	3.6	3.9	3.7
Flue Gas (wt.%)	1.2	1.3	1.3
H_2S (wt.%)	0.1	0.2	0.1
Gasoline (wt.%)	41.6	41.6	41.6
LPG (wt.%)	13.4	13.0	13.2
LCO (wt.%)	24.4	23.8	24.1
HCO (wt.%)	15.6	16.2	15.9

LPG=Liquefied petroleum gas; LCO=Light cycle oil; HCO= heavy cycle oil.

DCU can convert extract into light and middle distillates. Delayed coking is the processes where carbon is rejected to meet the requirement of hydrogen in distillate products. Properties of E-EPSRG suggest that DCU can be another potential option for extract utilization**.** It may important to mention that the metal content, carbondoson carbon residue (CCR) and viscosity of E-EPSG would be much lower in comparison to regular feed stocks such as vacuum residue (VR), thermal tar, pyrolysis tar and pitch streams to DCU. The lower viscosity and metal content of E-EPSG would improve the quality of coke generated. Further, it is vital to point out that coke formation in the DCU is the strong function of carbondoson carbon residue (CCR) value (Coke, wt.%=1.6×CCR) of feed stock (HPI, 2001). CCR value of E-EPSG (0.18%) is much lower than the CCR value of VR (varies in the range from 8.3 to 21.84%) (Kulkarni et al., 2010: Parra et al., 2010), one of the most commonly used feed stock in DCU. Lower CCR value of E-EPSG indicates that its blending with the regular feed stock of DCU will reduce the amount of coke formation and increase the distillate yield.

Chapter – 6

CONCLUSIONS AND RECOMMENDATIONS

6.1. CONCLUSIONS

On the basis of the result and discussion presented in chapters 3,4 and 5 for evaluation of solvents, solvent extractive desulfurization (SEDS) of straight run gas oil (SRGO) and various other gas oils, following major conclusions can be drawn:

6.1.1 Evaluation of Solvents

- A computational approach was used to establish new strategy for a more realistic screening of solvents for sulfur, nitrogen and aromatic compounds removal from gas oil using capacity, selectivity, performance index (P_I) and newly defined industrial usability index (S_{IUI}) which combined the capacity, selectivity and complexity of design and operation section for solvent recovery. These indices were estimated using the activity coefficient at infinite dilution.
- Twenty eight solvents comprising of six most widely used industrially proven conventional solvents and twenty two imidazolium based ionic liquids solvents were assessed and ranked based on above indices.
- Higher selectivity and capacity values of solvents for nitrogen compounds in comparison to sulfur suggests easier removal of nitrogen compounds.
- Rankings based on selectivity and capacity correlated well with the solubility parameter.
- P_I seemed to be better parameter than capacity and selectivity parameters, however, S_{IUI} was found to be more practical and realistic criteria for ranking of solvents.
- No single solvent ranked 1st for all sulfur and nitrogen compounds removal from gas oil. Therefore, the detailed sulfur component analysis in gas oil is necessary for selection of solvent.
- Overall, organic solvents were found to be better solvents than IL solvents for desulfurization and denitrogenation of gas oil and that the best solvent is the one which has moderate capacity and selectivity, and has lower boiling point than gas oil.

6.1.2 Desulfurization of Various Gas Oils

6.1.2.1 Straight run gas oil (SRGO)

- Five most wildly used organic solvents in hydrocarbon industry namely N-N-dimethyl formamide (DMF), N-N-dimethyl acetamide (DMA), acetonitrile (ACN), furfural and dimethyl sulfoxide (DMSO) were evaluated experimentally for sulfur removal from SRGO.

- Performance evaluation of these solvents was done in term of degree of sulfur removal (D_{sr}), yield (Y) of extracted SRGO, ESRGO (Y) and newly defined performance factor ($P_{f,\alpha}$) as a function of D_{sr}, Y and weight factor (α) to D_{sr} as: $P_{f,\alpha}$= $P_{f,\alpha}=\alpha D_{sr}+(1-\alpha)Y$.
- Nature of solvent, operating parameters such as solvent to feed S/F ratio and extraction temperature (T_E) and water content (W_c) in main solvent were found to significantly affect the the value of Y and D_{sr}.
- Operating conditions and W_c give huge process flexibility to relative maximization of Y and D_{sr} depending up on the need of secondary conversion process requirement to reduce the sulfur in ESRGO to ultra low level and to minimize loss of SRGO with extract and quality of extract to be used as carbon black feed stock (CBFS).
- DMF was found to be better solvent for SEDS of SRGO.
- Multi-response optimization with desirability function approach using three operational parameters namely W_c in DMF, S/F, and T_E were used as input variables for maximising two responses (yield of ESRGO and D_{sr}) which are highly important in the SEDS process.
- At the optimum values of variables (W_c=2.91 vol.%, S/F ratio=1.70 and T_E=46.4°C), yield of ESRGO (Y) and D_{sr} were found to be 81.67% and 60.53%, respectively.
- Y and D_{sr} values of 85.91% with 52.62% can be attained by using the optimized parameters when the importance to goal Y and D_{sr} were +++++ and ++ respectively, whereas respective Y and D_{sr} values were 67.49% and 77.39% when the respective importance were ++ and +++++.

6.1.2.2. Synthetic gas oil, SRGO, LCO and CGO

- Extraction of synthetic gas oil revealed that D_{sr} from gas oil strongly depends on molecular structure of sulfur compound and composition of carrier phase.
- D_{sr} values obtained after treatment of synthetic gas oil and actual SRGO with various solvents revealed that extraction study based on synthetic gas oil can be used for screening/ranking of the solvents for desulfurization. However, for implementation of SEDS process for gas oil in the actual industry, it is important to carry out some extraction studies on the actual gas oil with selected solvent to have an insight to be successful using performance parameters such as $P_{f,\alpha}$.
- Continuous counter current solvent extraction provided significantly better results for D_{sr} and $P_{f,\alpha}$ in comparison to single stage extraction. Raffinate produced from mixed gas oil (MGO) (mixture of SRGO, LCO and CGO in the ratio of 70:20:10) in continuous packed bed column extraction reduced sulfur, diaromatics and polyaromatics by 76.5% 93.5% and 95.2%, respectively

- Loss of paraffinic material with the extract hydrocarbon can be reduced to a great extent by generating the pseudo-raffinate from the extract phase with the help of antisolvent
- Pseudo-raffinate (which accounts 5-10% of feed) can be utilized in existing refinery processes such as hydrocracker and fluidized catalytic cracker (FCC) units to generate the distillate products with reduced sulfur content to diminish the severity of hydrotreater for cost effective production of low sulfur gas oil.
- 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.
- Generated extract can also be used as blending stock in rubber processing oil, fuel oil blending stream. It can also be routed to fluid catalytic cracker unit (FCCU), delayed coking unit (DCU) to convert it into light and middle distillates.
- It seems that the integrated process may be overall more economical than the single or multi stage hydrotreatment processes to be operated at very severe operating conditions to meet the strict sulfur and cetane number of transported gas oil.
- A schematic of conceptualized strategy used in this study for the removal of sulfur and aromatic compounds from various gas oil streams using solvent extraction and utilization of extract stream is shown in Figure 6.1.

6.2 RECOMMENDATIONS

Based on the present study, following studies are proposed for future work:

- Study for quantitative effect of extractive desulfurization on the performance improvement of hydrodesulfurization (HDS) process.
- Study of combination of different desulfurization methods such as extractive desulfurization followed by HDS or oxidative desulfurization (ODS) or adsorptive desulfurization (ADS) to reduce the sulfur to ultra low level in cost effective way.
- To generate the fundamental correlation for estimating the operating conditions for maximizing the D_{sr} and Y by carrying out extensive extraction study with various actual and synthetic gas oils to handle the problem associated with the change in composition of actual gas oil in refinery.
- To design temperature swing solubility based solvent for reducing the energy requirement in the conventional solvent recovery section due to involvement of main or secondary solvent vaporization.

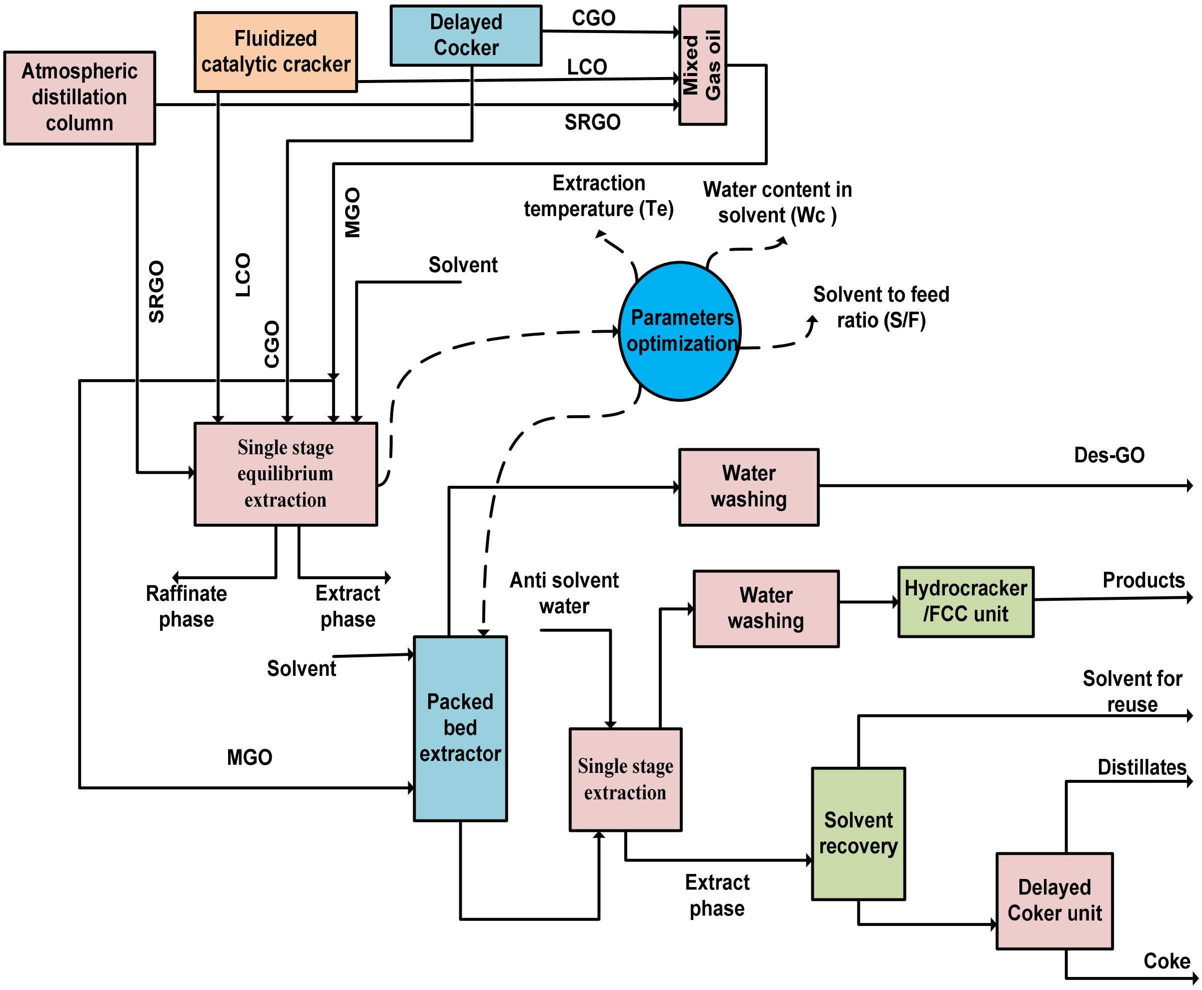


Figure 6.1. Schematic of novel strategy for removal of sulfur and aromatic compounds from various gas oil streams and extract utilization. SRGO: Straight run gas oil; LCO: Light cycle oil; CGO: Coker gas oil; Des-GO: Desulfurized gas oil (raffinate); FCC: Fluidized catalytic cracking.

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