



## Full Length Article

## Desulfurization of gas oil using a distillation, extraction and hydrotreating-based integrated process

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## ABSTRACT

In the present study, an integrated process (IP) was conceptualized for carrying out the deep desulfurization of gas oil (GO) in a cost-effective and environment-friendly way. This IP is based on the best salient features of distillation, solvent extraction, and hydrotreating processes. The practical applicability of the IP is illustrated using experimental data and estimated responses. The proposed IP can produce gas oil containing 73 ppmw compared to 328 ppmw sulfur produced using standalone hydrotreating process (SHP) from GO having sulfur 1.36% under same operating conditions of temperature and pressure, catalyst, and catalyst loading in hydro-treating reactor. The chemical hydrogen consumption of IP was found to be 48.1% less compared to SHP for the same concentrations of sulfur and aromatic in treated gas oil. Overall, 95.6% of GO can be converted into low sulfur gas oil using mild operating conditions in hydrotreating zone of IP. Rest 4.4% hydrocarbons of SRGO can be used either as valuable carbon black feedstock or feed to delayed coking unit or as aromatic rich rubber processing solvent.

## 1. Introduction

There is continuously increasing trend of producing ultraclean gas oil with strict specifications of sulfur and polyaromatics. This is important to reduce the exhaust emissions such as oxides of sulfur (SO<sub>x</sub>), oxides of nitrogen (NO<sub>x</sub>), unburnt hydrocarbon compounds (HC) and particulate matter (PM). Moreover, this shall also facilitate the implementation of advanced emission control technologies in automobiles which performance affects adversely with the presence of sulfur in fuel [1–5]. Hydrotreating is the most commonly used process in the refinery for removal of sulfur and polyaromatics from gas oil [6]. The sulfur species present in gas oil include sulfides, thiols, thiophenes, benzothiophene, dibenzothiophene, benzonaphthothiophene with and without alkyl substituents [7]. The rate of hydrodesulfurization strongly depends on the structure of a sulfur compound. The relative reaction rates of major sulfur compounds found in gas oil have been tabulated in Table 1 [8]. It is clear that dibenzothiophenes and dibenzonaphthothiophene and their alkyl substituents are highly refractive sulfur compounds for desulfurization [9]. Moreover, condensed polyaromatics in gas oil inhibit the desulfurization of refractive sulfur compounds significantly due to competitive adsorption of aromatics on active sites of catalyst [5]. The inhibition effect shall be more

pronounced in deep desulfurization due to the very low relative concentration of sulfur compounds compared to polyaromatic compounds. Therefore, production of ultra-low sulfur gas oil using hydrotreating shall lead to the drastic increase in the severity of operating conditions, purity of hydrogen and catalyst volume etc. in standalone hydrotreating process (SHP).


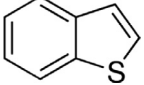
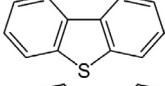
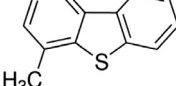
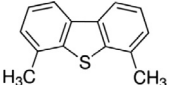
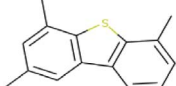
Retrofitting of existing hydrotreating unit for deep desulfurization shall include integration of new high-pressure reactor with an existing reactor. Others retrofitting modifications shall include incorporation of new circulating hydrogen gas purification system, re-engineering of reactor internals configuration, new hydrogen makeup compressor to meet the requirement of significant increase in hydrogen consumption, recycle gas compressor due to increased recycle gas flow and higher pressure drop, vessels sizes to address hydraulic issues, and revamp of an amine treating unit for the treating the additional gas rate [9]. Moreover, there shall be a need for either installation of new grass root hydrogen plant or capacity enhancement of existing H<sub>2</sub> plant to meet the significant increase in H<sub>2</sub> consumption during deep desulfurization [10–12]. Therefore, deep desulfurization of gas oil using SHP shall need massive capital investment and high operating cost. It will also lead generation of large quantity of greenhouse gas (GHG) emission to the environment. Thereby, refiners are seriously looking for alternative

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Nomenclature			
<i>Acronym</i>			
ADS	selective adsorptive desulfurization	PsePH	pseudo extract phase hydrocarbon
BDS	biodesulfurization	RHFGo	raffinate of HFGo
BmCI	bureau of mines correlation index	RHFGo	raffinate of HFGo
CBFS	carbon black feed stock	SED	solvent extraction desulfurization
Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	cobalt nitrate	SHP	stand-alone hydrotreating process
DMDS	dimethyl disulfide	SiC	silica carbide
DMF	N-N-dimethyl formamide	SO <sub>x</sub>	oxides of sulfur
EPH	extract phase hydrocarbon	SRGo	straight run gas oil
EPoCE	extract phase of continuous extraction	WHSV	weight hour space velocity
EPHoCE	extract phase hydrocarbon of continuous extraction	XRF	X-ray fluorescence
H <sub>3</sub> PO <sub>4</sub>	phosphoric acid	γ-Al <sub>2</sub> O <sub>3</sub>	Gamm alumina
HC	unburnt hydrocarbon compounds		
HCS	hydrodynamic cavity desulfurization	<i>Notations</i>	
HFGo	heavy fraction of gas oil	BT	benzothiophenic sulfur% of total sulfur
HOR	hydrogen to oil ratio	D <sub>ar</sub>	degree of aromatic removal
HPS	high pressurized gas–liquid separator	DBT	dibenzothiophenic sulfur% of total sulfur
IBP	initial boiling point	D <sub>sr</sub>	degree of sulfur removal
ICP-AES	inductively coupled plasma atomic emission spectroscopy	H <sub>HAS</sub>	hydrogen consumption for aromatic saturation
IP	integrated process	H <sub>HDS</sub>	hydrogen consumption for desulfurization
LFGO	light fraction of gas oil	HP <sub>F</sub>	hydrotreating performance factor
LFRHFGo	mixture of LFGO and RHFGo	M <sub>w</sub>	molecular weight of feed and distillates
LPS	low pressurized gas–liquid separator	S	sulfur
(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> ·4H <sub>2</sub> O	ammonium heptamolybdate	S/F	solvent to feed ratio
Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	nickel nitrate	S <sub>T</sub>	denotes targeted sulfur content
NO <sub>x</sub>	oxides of nitrogen	T <sub>b</sub>	normal boiling point
ODS	oxidative desulfurization	T <sub>E</sub>	extraction temperature
PFPD	pulsed flame photometric detector	Y%	raffinate yield, volume%
PM	particulate matter	ρ	density @ 20 °C, kg/l.
PseEP	pseudo extract phase	<i>Subscript</i>	
PseRP	pseudo raffinate phase	F	factor
PseR	pseudo raffinate	f	feed
		p	product

**Table 1**  
Relative rate of hydrodesulfurization of sulfur compounds [8].

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

cost-effective, a flexible and environment-friendly process for deep desulfurization of gas oil.

Many researchers are working on alternative desulfurization methods such as oxidative desulfurization (ODS) [13–16], selective adsorptive desulfurization (ADS) [9,17–19], biodesulfurization (BDS) [20–21], and solvent extraction desulfurization (SEDS) [22–28], hydrodynamic cavitation desulfurization (HCS) [29]. Despite enormous academic research was carried out in the area of ODS, ADS, BDS, HCS, SEDS, there is a long way to cover for their large-scale commercialization in the refinery due to the association of various challenges with these processes. ODS is a multi-step process and there are issues related to an expensive oxidant, reaction selectivity, safety, equipment cost. ADS has the salient feature of low-temperature operation. However, development of adsorbents having high adsorption capacity and high selectivity for adsorption of aromatic sulfur compounds in presence of high concentration of nonsulfur aromatic compounds, cost-effective regeneration of adsorbent are some of the major challenges with ADS [30]. Moreover, despite of environment friendly nature of BDS, various challenges such as slow rate of desulfurization, the requirement of a large quantity of microorganism (biomass to sulfur ratio ~ 2.5 g/g), the performance of biological systems under variable conditions of pH, dissolved oxygen and temperature etc. need to be addressed for BDS process commercialization [31–33]. HCS process does not require a catalyst and seems attractive. However, this process is also under development stage. SEDS process cannot bring the sulfur to a very low ppmw level. The amount of dissolved hydrocarbon in extract phase also increased with a decrease in target value of sulfur in extracted gas oil. However, solvent extraction involves only physical separation and does

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