Kinetics of Hydrodesulphurization of Diesel: Mass Transfer Aspects

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Abstract—In order to meet environmental norms, Indian fuel policy aims at producing ultra low sulphur diesel (ULSD) in near future. A catalyst for meeting such requirements has been developed and kinetics of this catalytic process is being looked into. In the present investigations, effect of mass transfer on kinetics of ultra deep hydrodesulphurization (UDHDS) to produce ULSD has been studied to determine intrinsic kinetics over a pre-sulphided catalyst. Experiments have been carried out in a continuous flow micro reactor operated in the temperature range of 330 to 360^0C, whsv of 1 hr^{-1} at a pressure of 35 bar, and its parameters estimated. Based on the derived rate expression and estimated parameters optimum operation range has been determined for this UDHDS catalyst to obtain ULSD product.

Keywords—Diesel, hydrodesulphurization, kinetics, mass transfer.

I. INTRODUCTION

TRANSPORTATION fuels are facing current changes driven by environmental constraints worldwide. Lowering of sulphur in diesel is a worldwide trend. The main aim is to decrease sulphur oxides produced from vehicle engines and to improve catalytic converter's yields [1]. On similar lines, Indian fuel policy aims at achieving 350 ppm diesel by 2010 nationwide and below 50 ppm in selected cities [2]. Desulphurization rates are strongly related to substituent groups present in the ring. The most refractory sulphur species identified include alkyl substituted dibenzothiophenes (DBT), particularly alkyl groups adjacent to sulphur atom causing steric hindrance [3]. The UDHDS process mainly intends to convert these refractory substituted DBTs. The choice between Co-Mo and Ni-Mo UDHDS catalyst formulations is dependent on the nature of sulphur present in diesel. For removal of non refractory sulphur, the one which contains lesser amount of DBTs, Co-Mo catalysts are generally preferred at low and medium operating pressures. Ni-Mo formulations are preferred when heavier sulphur molecules need to be processed by following the hydrogenation route requiring higher operating pressures and leading to simultaneous aromatics saturation also [4]-[7]. The optimum choice of catalyst could be Co-Mo supported with Ni when hydrogen consumption in the refinery is a bottle neck [7]. Keeping in view the hydrogen economy and national fuel policy a UDHDS catalyst of Co-Mo-Ni type has been developed [8] for bringing down the sulphur in diesel from around 2000 ppm to 50 ppm.

Successful use of this catalyst at a commercial scale would

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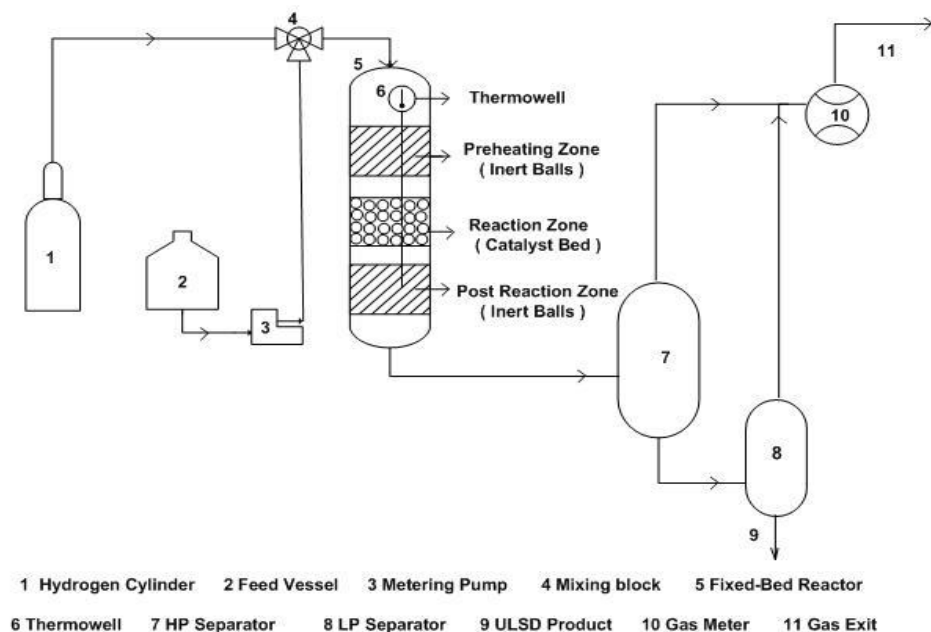
require development of a kinetic model. Conventionally, HDS kinetic modeling was often limited to simple power law which ignored the effect of mass transfer on kinetics. If the conversion of sulphur has to be close to 1 to satisfy environmental regulations rate expressions without mass transfer effects will be inadequate and therefore would lead to unreliable design and operation of reactors. An attempt has been made to derive rate expressions including mass transfer effects in terms of total sulphur and estimate intrinsic rate parameters so that conversion can be predicted with better accuracy. Experimental studies using this catalyst have been carried out in a flow micro reactor in the temperature range of 330-360^0C, at whsv of 1 hr^{-1} and pressure of 35 bar.

II. EXPERIMENTATION SECTION

The straight run diesel feed used in the present investigation was obtained from a refinery. Properties of SR diesel and catalyst used are summarized in Table I & II. The catalyst was pre-sulphided with DMDS.

TABLE I
CHARECTERISTICS OF DIESEL OIL

Parameters	QUANTITY	Units
Total sulphur	1700	ppm
Density at 15^0C	0.8509	kg/dm^3
Boiling Range	156-360	^{0}C

TABLE II
PHYSICAL PROPERTIES OF CATALYST

Parameters	QUANTITY	Units
Surface area	230.8	m^2/g
Shape	cylindrical	n.a
Average diameter	1.5	mm
Average length	3.0	mm

The schematic diagram of the micro reactor unit is shown in Fig. 1. Hydrogen is supplied from the cylinder (1). Diesel feed is pumped in metered quantity from the feed vessel (2) by a metering pump (3). These are mixed in a mixing block (4) before being introduced to the reactor (5). The reactor is a fixed bed of tubular type made of stainless steel with coaxial thermocouple tube (6) along its length to measure temperature at different positions inside the reactor. The reactor has three independent zones heated by three cylindrical furnaces and its temperature is regulated by a thermostatic control system. The top zone is the preheating zone, the middle zone is the reaction zone followed by the post reaction or bottom zone. The middle

Fig. 1 Experimental setup

| 1 Hydrogen Cylinder | 2 Feed Vessel | 3 Metering Pump | 4 Mixing block | 5 Fixed-Bed Reactor |
| 6 Thermowell | 7 HP Separator | 8 LP Separator | 9 ULSD Product | 10 Gas Meter | 11 Gas Exit |

zone is loaded with the catalyst. The top zone of the reactor bed has been loaded with inert alpha-alumina balls, which is a packing material primarily for preventing mal distribution of the feed. To improve the contacting between feed and catalyst, SiC is used as a diluent.

The hydro treated diesel is separated from gases in two stages, first in a high pressure separator drum (7) followed by a low pressure separation drum (8). The gases are collected and metered through a gas meter (10) and the hydro treated liquid product (9) is collected from the bottom of the low pressure separator drum (8). The experimental runs are accomplished in the temperature range of $330\text{-}360^0$ C, whsv of 1 hr^{-1} at 35 bar and at hydrogen to hydrocarbon ratio of 750 N dm^3/dm^3. The total sulphur in feed and product samples have been analyzed by total sulphur analyzer TS 3000 based on UV Florescence principle.

III. RESULTS AND DISCUSSION

The micro reactor has been modeled as a plug flow reactor (PFR). The nomenclatures used have been described in Table III. Mole balance has been carried across a differential shell element of Δz, length and of cross sectional area, A and numerically integrated over the reactor length, L to obtain the final conversion, X_A. The reactor id being small and the length of the shell is infinitesimal, it is assumed that no radial/axial gradient of concentration/temperature exists within this differential shell element. The axial temperature variation across the reactor is never greater than 5^0C hence, considered as an isothermal process. Based on these assumptions the differential shell mole balance is derived as shown below:

In - Out + Generation = Accumulation

$$F_A\big|_Z - F_A\big|_{Z+\Delta z} + r_A \Delta V = \frac{\Box \acute{N}_A}{\Box t \acute{Y}} \tag{1}$$

where,

$$\Delta V = A\Delta z(1-\varepsilon) \tag{2}$$

At steady state,

$$\frac{\Box \acute{N}_A}{\Box t \acute{Y}} = 0 \tag{3}$$

Hence,

$$\frac{dF_A}{dz} = r_A A(1-\varepsilon) \tag{4}$$

In terms of conversion,

$$F_{A0}\frac{dX_A}{dz} = -r_A A(1-\varepsilon) \tag{5}$$

Due to high H_2/HC ratio, vfrac is close to 1 in the operating range, hence the reaction has been considered as gas-solid reaction. It is assumed that at steady state, the film surrounding the catalyst offers resistance to the transfer of the reactant sulphur molecule diffusing from the bulk to the surface of the catalyst [9]. The second resistance is offered to the molecule while it diffuses from the surface to the reactive site inside the pores expressed as effectiveness factor, η. The UDHDS process kinetics has been assumed to be linear with respect to sulphur concentration, C_A [10]. The basic mole balance ("5") is thus modified after incorporating these mass transfer resistances as shown in "6-7". The effect of total pressure on rate expression was studied earlier for the UDHDS catalyst [8], [11] and has been incorporated while developing the rate expression ("7").

TABLE III
NOMENCLATURE

Symbol	Description	Units
a	external catalyst surface area per unit reactor volume	cm^2/cm^3
A	cross-sectional area of the PFR	cm^2
C	concentration	$mmol/cm^3$
d_s	equivalent spherical diameter of catalyst particle	cm
E	activation energy	cal/mol
F	molar flow	mmol/hr
h	elemental thickness of the differential PFR shell	cm
k	specific reaction rate including pressure effect	hr^{-1}
k_0	frequency factor	$hr^{-1} bar^{-0.5}$
k_c	mass transfer coefficient	cm/hr
k_r	specific reaction rate	$hr^{-1} bar^{-0.5}$
L	length of the PFR	cm
N_{PFR}	number of differential shell elements in the PFR	
N	number of moles accumulated	mmol
p	total pressure	bar
q	number of experimental data points in error calculations	
-r	rate of disappearance per unit volume	$mmol/(cm^3 hr)$
R	Ideal gas constant	cal/(mol K)
t	time	hr
T	temperature	K
V	volume	cm^3
X	conversion	
z	distance from the reactor inlet	cm

Subscripts

0	at initial condition (t=0)	
A	limiting reactant, sulphur	
i	shell element number varying from 1 to N_{PFR}	
j	experimental data points varying from 1 to q	
z	face of the shell element of thickness Δz located at distance z from the reactor inlet	
eff	effective	

Superscripts

e	experimental	
p	predicted	

Greek symbols

φ	objective function	
∂	partial differential	
ε	void fraction	
Δ	infinitesimal change	
$\Delta 1$	error percent	
η	effectiveness factor	

$$F_{A0} \frac{dX_A}{dz} = -r_{eff} A(1-\varepsilon) \tag{6}$$

where,

$$-r_{eff} = \eta \cdot \frac{k_r \cdot p^{0.50} \cdot k_c \cdot a}{\eta \cdot k_r \cdot p^{0.50} + k_c \cdot a} \cdot C_A \tag{7}$$

The mass transfer coefficient, k_c and effectiveness factor, η have been determined by standard procedures [12]-[14]. The physical parameters like density, viscosity, diffusivity required for the computations of k_c and η have been estimated by standard methodologies [15]. The mole balance ("6") has been

numerically solved by Euler's method [16]. The PFR has been divided into N_{PFR} elements of uniform thickness h defined in "9". The value of X_A of $i+1^{th}$ element is computed from i^{th} element using the algorithm expressed in "8". Nelder-Mead simplex technique [17] has been used for estimating the kinetic parameters by minimizing the objective function, φ. The function φ, has been defined as a summation of absolute values of the scaled conversion terms ("10"). The extent of fit is computed in terms of error percent, $\Delta 1$ ("11").

$$X_A \Big|_{i+1} - X_A \Big|_i = \frac{dX_A}{dz} \Big|_i . h \tag{8}$$

where,

$$h = \frac{L}{N_{PFR}} \tag{9}$$

$$\varphi = \sum_{j=1}^{q} \left| \frac{X_{Aj}^e - X_{Aj}^p}{X_{Aj}^e} \right| \tag{10}$$

$$\Delta 1 = \frac{100}{q} \sum_{j=1}^{q} \left| \frac{X_{Aj}^e - X_{Aj}^p}{X_{Aj}^e} \right| \tag{11}$$

The simulations have been carried out based on data given in Table IV & V. The simulated results are reported in Table VI. The extent of fits, $\Delta 1$ have been found to be less than 0.15 in all the cases. The magnitudes of $k_c a$ obtained are of the order of 10^4 which are much larger as compared to k_r a value, "7" is thus simplified to "12". The low magnitudes of effectiveness factor, η and high magnitudes of $k_c a$ indicate, external resistance is low and internal resistance is controlling.

$$-r_{eff} = \eta \cdot k_r \cdot p^{0.50} \cdot C_A \tag{12}$$

On rearrangement,

$$-r_{eff} = \eta \cdot k \cdot C_A \tag{13}$$

Based on rate constants, k ("13") the activation energy and frequency factor have been obtained to be 9.31 kcal/mol and 1.1743×10^5 hr^{-1} respectively. The frequency factor, k_0 may

TABLE IV
INPUT DATA

Parameters	*QUANTITY*	Units
a	17.4	cm^{-1}
A	0.8509	cm^2
C_{A0}	0.4502	$mmol/cm^3$
F_{A0}	0.3187	mmol/hr
ε	0.37	n.a
h	8.8×10^{-4}	cm

TABLE V
EXPERIMENTAL CONDITIONS

Expt. Conditions	Pressure bar	Temp K	whsv hr^{-1}	X_A^{exp}
1	35	603	1	0.9572
2	35	613	1	0.9680
3	35	623	1	0.9706
4	35	633	1	0.9809

alternately be expressed as a function of total pressure ("14"). The activation energies computed based on lumped parameter approach for different sulphur molecules in diesel are reported to be in the range of 22-53 kcal/mol [10].

TABLE VI
SIMULATED PARAMETERS

Expt. Conditions	$k_c a$ hr^{-1}	k_r $hr^{-1}bar^{-0.50}$	k hr^{-1}	η
1	3.64×10^4	8.15	48.22	0.066
2	3.75×10^4	9.26	55.88	0.0623
3	3.85×10^4	10.47	57.03	0.0626
4	3.97×10^4	11.77	69.79	0.0574

This difference may be attributed to lumping of mass transfer effects with kinetics and partly due to higher activity of the UDHDS catalyst. Therefore, considering intrinsic kinetics is essential for scale up and design of industrial reactors especially, when we are targeting for ULSD levels.

$$k_0 = 1.9849 \times 10^4 . p^{0.50} \qquad (14)$$

After incorporating "14" k is redefined,

$$k = 1.9849 \times 10^4 . p^{0.50} . e^{\frac{-9310}{RT}} \qquad (15)$$

The effect of total pressure on conversion at 360^0C has been simulated (Fig. 2) using the parameters in Table VI. It is evident from the trend that a pressure of 40 bar is optimum for the operation of the UDHDS catalyst. Further, the conversion profile has been simulated over a range of whsv and temperature at optimum this pressure of 40 bar (Fig. 3) to determine acceptable range of operating parameters for producing ULSD. Thus, to achieve ULSD, the reactor should be operated at or below whsv 1 hr^{-1} and above temperature of 350^0C.
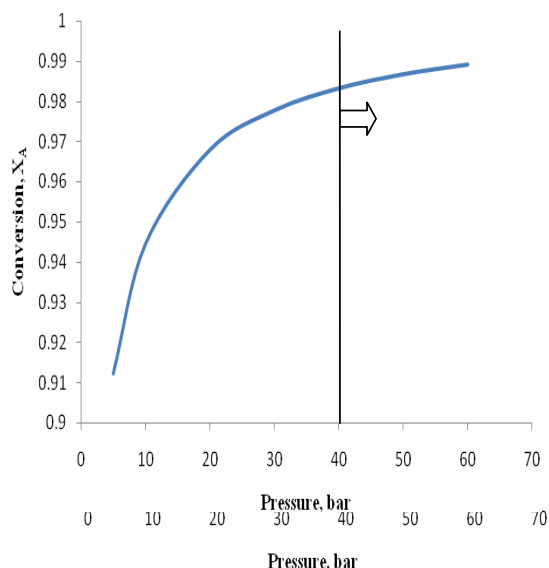

Fig. 2 Simulated effect of pressure on Conversion at 360^0C

There is a worldwide trend to further reduce the sulphur in diesel to 15 ppm or lower. Use of novel catalyst supports by modification of conventional gamma-alumina, addition of zeolites and/or of mixed oxides seems to hold great potential for further improvement in catalyst performance [8].
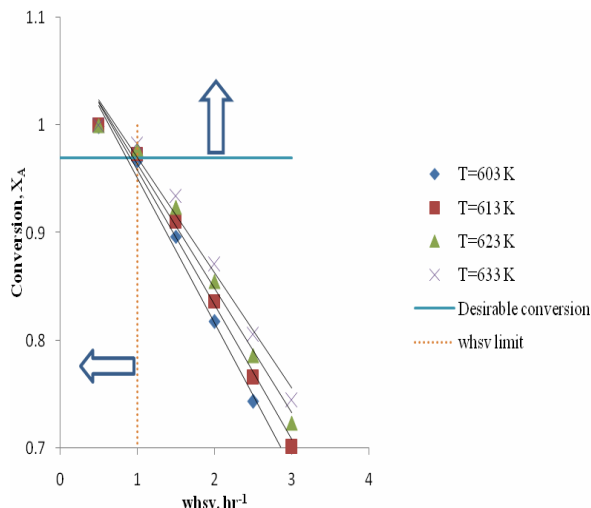

Fig. 3 Simulated conversion profile at a total pressure of 40 bar. The straight lines represent the trend lines

Inspite of the highly active UDHDS catalyst, we may still fail to meet ULSD specifications if the design of the reactor internals does not provide near-ideal gas/liquid distribution. As sulphur targets approaches zero even small amount of bypassing the catalyst would result in a very critical decline in performance. New reactor internals like distributors have been designed to afford near ideal fluid distribution for optimum catalyst utilization. Improper distribution of the reactants over the catalyst will contribute to channeling through the catalyst bed resulting in inefficient utilization of the catalyst, resulting in development of hot spots, premature catalyst deactivation and failure to attain ULSD levels [4], [5], [18].

IV. CONCLUSION

The salient conclusions from this study are:
- It is feasible to produce ULSD using this UDHDS catalyst at whsv at or below 1 hr^{-1} above 350^0C and optimum pressure of 40 bar.
- It is evident from the present study that the UDHDS kinetics is pore diffusion controlled. To improve conversions it is desirable to improve effective pore diffusivity. This may be achieved by modifying catalyst parameters like size, porosity and tortuosity.

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