



Modeling the kinetics of parallel thermal and catalytic hydrotreating of heavy oil



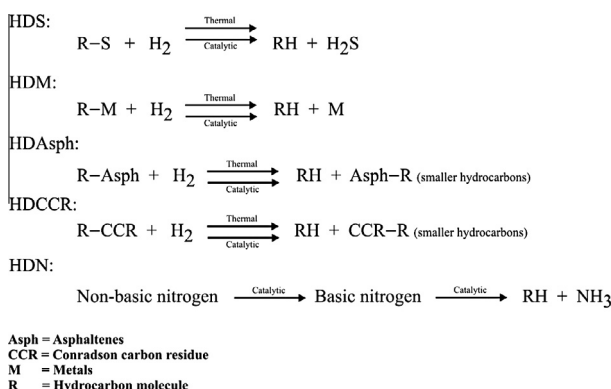
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HIGHLIGHTS

- Kinetics of parallel thermal and catalytic HDT was derived from CSTBR experiments.
- HDS, HDN (basic and non-basic), HDM, HDAsph and HDCCR reactions were modeled.
- Time-dependant catalyst deactivation function was incorporated into kinetic model.
- Catalytic reactions occur mostly at low severity reaction conditions.
- At high severity conditions thermal reactions are more favored.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of experiments were performed for obtaining the kinetics of the parallel thermal and catalytic hydrotreating reactions. The reactions considered were: hydrodesulfurization, hydrodenitrogenation (basic and non-basic), hydrodemetallization, hydrodeasphaltenization and hydro Conradson carbon removal. Hydrodesulfurization reaction was described by Langmuir–Hinshelwood kinetics while the other reactions were modeled with power-law approach. The tests were carried out in a CSTBR at the following conditions: 380–420 °C, 9.8 MPa, 891 std m³/m³ of hydrogen-to-oil ratio, 0.98–2.56 of g feed/(g cat h), and 200 h of time-on-stream. The developed kinetic model incorporates the effectiveness factor and a time-dependant deactivation function for obtaining the intrinsic kinetic parameters. It was demonstrated that at low severity reaction conditions the reactions occur via catalytic route, while at high severity conditions thermal reactions are more favored.

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1. Introduction

The upgrading of heavy and extra-heavy crude oils characterized by high impurities content (sulfur, nitrogen, asphaltenes, Conradson carbon residue, and metals) has attracted more attention of refiners to cover the demand of more valuable products such as

gasoline, kerosene, jet fuel and diesel. Hydrotreating and hydrocracking are still the most preferred technologies for upgrading of heavy oils. Various advances have been advised in terms of reactor design, process configuration and catalyst formulations. In parallel, kinetic models have been developed with several levels of sophistication using different catalyst, feeds, reactors and reaction conditions. Most of the experimental studies have been carried out at steady-state conditions and only a few have been conducted during the initial period of deactivation of the catalyst.

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Nomenclature

A_{C_i}	Arrhenius pre-exponential factor for catalytic kinetic constants (h^{-1})	$k_{T_{Ni}}$	thermal kinetic constant for the HDNi reaction ($\text{ppm}^{0.350} \text{h}^{-1}$)
A_{d_i}	Arrhenius pre-exponential factor for deactivation constants (h^{-1})	k_{T_V}	thermal kinetic constant for the HDV reaction ($\text{ppm}^{0.487} \text{h}^{-1}$)
A_{H_2S}	van't Hoff pre-exponential factor for hydrogen sulfide adsorption constant ($\text{cm}^3 \text{mol}^{-1}$)	k_{T_S}	thermal kinetic constant for the HDS reaction ($\text{wt}\%^{0.062} \text{h}^{-1}$)
A_{T_i}	Arrhenius pre-exponential factor for thermal kinetic constants (h^{-1})	m_i	deactivation order for the reaction i
C_{Asph}	asphaltenes content (wt%)	m_{T_0}	total mass flow (g h^{-1})
C_{BN}	basic nitrogen content (ppm)	n_{C_i}	reaction order of the catalytic reaction rate i
C_{H_2}	hydrogen concentration (mol cm^{-3})	n_{T_i}	reaction order of the thermal reaction rate i
C_i	content of the compound i at the reactor outlet	R	universal gas constant ($\text{kcal mol}^{-1} \text{K}^{-1}$)
$C_{i,0}$	content of the compound i at the reactor inlet	T	temperature (K^{-1})
C_{H_2S}	hydrogen sulfide concentration (mol cm^{-3})	t	time-on-stream (h)
C_{NBN}	non-basic nitrogen content (ppm)	$(-r_{HDCCR})$	HDCCR reaction rate ($\text{wt}\% \text{h}^{-1}$)
C_{Ni}	nickel content (ppm)	$(-r_{HDAsph})$	HDAsph reaction rate ($\text{wt}\% \text{h}^{-1}$)
C_V	vanadium content (ppm)	$(-r_{HDNBN})$	HDNB reaction rate (ppm h^{-1})
C_S	sulfur content (wt%)	$(-r_{HDNBN})$	HDNNBN reaction rate ($\text{ppm}\% \text{h}^{-1}$)
Ea_{C_i}	activation energy for the catalytic reactions (kcal mol^{-1})	$(-r_{HDNi})$	HDNi reaction rate (ppm h^{-1})
Ea_{T_i}	activation energy for the thermal reactions (kcal mol^{-1})	$(-r_{HDS})$	HDS reaction rate ($\text{wt}\% \text{h}^{-1}$)
E_{d_i}	deactivation energy for the reaction i (kcal mol^{-1})	$(-r_{HDV})$	HDV reaction rate (ppm h^{-1})
ΔH_{ads}	enthalpy of adsorption of hydrogen sulfide (kcal mol^{-1})	W_{Cat}	weight of catalyst (g)
$k_{C_{Asph}}$	catalytic kinetic constant for the HDAsph reaction ($\text{wt}\%^{-0.503} \text{h}^{-1}$)	$WHSV$	weight hourly space velocity (h^{-1})
$k_{C_{BN}}$	catalytic kinetic constant for the HDNBN reaction ($\text{ppm}^{-0.792} \text{h}^{-1}$)		
k_{C_i}	catalytic kinetic constant for the reaction i		
$k_{C_{NBN}}$	catalytic kinetic constant for the HDNNBN reaction ($\text{wt}\%^{-1.154} \text{h}^{-1}$)		
$k_{C_{Ni}}$	catalytic kinetic constant for the HDNi reaction ($\text{ppm}^{-1.406} \text{h}^{-1}$)		
k_{C_V}	catalytic kinetic constant for the HDV reaction ($\text{ppm}^{0.290} \text{h}^{-1}$)		
k_{C_S}	catalytic kinetic constant for the HDS reaction ($\text{wt}\%^{-0.503} \text{h}^{-1}$)		
k_{d_i}	deactivation constant for the reaction i (h^{-1})		
K_{H_2S}	adsorption-equilibrium constant for the hydrogen sulfide ($\text{cm}^3 \text{mol}^{-1}$)		
$k_{T_{Asph}}$	thermal kinetic constant for the HDAsph reaction ($\text{wt}\%^{0.795} \text{h}^{-1}$)		
$k_{T_{BN}}$	thermal kinetic constant for the HDNBN reaction ($\text{ppm}^{0.137} \text{h}^{-1}$)		
k_{T_i}	thermal kinetic constant for the reaction i		
$k_{T_{NBN}}$	thermal kinetic constant for the HDNNBN reaction ($\text{ppm}^{0.137} \text{h}^{-1}$)		
		Greek symbols	
		η	effectiveness factor
		\varnothing	catalyst activity
		Subscripts	
		<i>HDS</i>	hydrodesulfurization
		<i>HDNi</i>	hydrodenickelation
		<i>HDV</i>	hydrodevanadization
		<i>HDAsph</i>	hydrodeasphaltenization
		<i>HDCCR</i>	hydro-Conradson carbon residue conversion
		<i>HDNNBN</i>	hydrodenitrogenation of non-basic nitrogen
		<i>HDNBN</i>	hydrodenitrogenation of basic nitrogen
		<i>i</i>	S, Ni, V, Asph, CCR, NBN, BN
		<i>Asph</i>	asphaltenes
		<i>BN</i>	basic nitrogen
		<i>CCR</i>	Conradson carbon residue
		<i>NBN</i>	non-basic nitrogen
		<i>Ni</i>	nickel
		<i>S</i>	sulfur
		<i>V</i>	vanadium

Different kinetic studies have been reported for hydrotreating of oil fractions, and are well documented in the literature [1], but only a few deal with the parallel catalytic and thermal hydrotreating reaction [2–5]. Because vacuum gas oil has been mostly used as feed, catalyst deactivation has been neglected.

It has also been reported that catalytic reactions may compete and/or be coupled with thermal reactions, where the latter produce reactive free radicals by breaking C–C, C–H and C–heteroatom bonds. During thermal cracking high molecular weight species are converted to lower molecular weight species, which are more accessible to the active surface of the catalyst through the pores. Therefore, thermal and catalytic reactions act sequentially via thermal scission and hydrogenation. This occurs because catalysts promote hydrogenation of aromatic rings and opening of those rings occurs by either thermal reactions or reactions catalyzed by acidic sites [2].

Gollakota et al. [3] studied the direct liquefaction of coal in a batch micro reactor in the presence of a coal-derived solvent, hydrogen gas, and a Co-Mo/Al₂O₃ supported catalyst. It was concluded that a combination of catalytic and thermal reactions may be involved in the direct coal liquefaction.

Khorasheh et al. [4] have reported that sulfur can be removed from coker gas oil by thermal hydrocracking reactions when operating at high temperature (420–450 °C). Gray et al. [6] have also proposed that low conversions of sulfur compounds in vacuum residues from different sources can be achieved by hydrothermal reactions over γ -alumina.

Sanford [7] suggested that the CCR conversion route is initiated by thermal bond cleavage, after that a catalytic hydrogenation route will lead to the CCR conversion through the hydrogenation of molecules which could be subsequently decomposed by a thermal route to give gas and distillates.

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