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Full Length Article

Kinetic parameter estimation and simulation of trickle-bed reactor for hydrodesulfurization of whole fraction low-temperature coal tar

Xian Feng[a], Dong Li[a,*], Junghui Chen[b,*], Menglong Niu[c], Xu Liu[a], Lester Lik Teck Chan[b], Wenhong Li[a]

[a] School of Chemical Engineering, Northwest University, Xi'an 710069, People's Republic of China
[b] Department of Chemical Engineering, Chung-Yuan Christian University, Chung-Li, Taoyuan 32023, Taiwan, ROC
[c] School of Chemistry and Chemical Engineering, Xi'an Shiyou University, Xi'an 710065, People's Republic of China

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ABSTRACT

With whole-fraction low temperature coal tar (LTCT) as raw material, which boiling point range is 209–514 °C. This paper conducts hydrotreatment (HDT) test for 1176 h on trickle-bed reactor (TBR) with commercial NiMo/Al_2O_3-SiO_2 catalyst. The reaction conditions are as follows: reaction temperature 613–653 K, reaction pressure 10–14 MPa, liquid hourly space velocity (LHSV) 0.2–0.4 h^{-1}, and hydrogen-to-oil volume ratio 1000:1. Considering the short life of coal tar HDT catalyst, a kinetic model of whole-fraction LTCT hydrodesulfurization (HDS) including running time (t_1) and catalyst half-life (t_c) was established. The kinetic parameter estimation was conducted according to the experimental data, and the results are as follows: activation energy 94965 J/mol, reaction order 1.5, and the relative error of the model is less than 5%.

Based on the premise of steady state operation, the HDS reaction happened in the three-phase trickle-bed reactor was simulated by combining the mass transfer, reaction kinetics model and physical property data of LTCT. The results show that the experimental and simulated values of sulphur content at the exit of the reactor are within the error range of 5%. By simulating the whole-fraction LTCT HDS reactor, the pattern of changes in the concentrations of hydrogen sulfide, hydrogen and sulfur in gas, liquid and solid phases according to the length of the reactor were obtained. Based on this, this paper discusses on the impacts of each process parameter and hydrogen sulfide partial pressure on LTCT HDS, and works out the reaction characteristics of whole-fraction LTCT HDS different from crude oil fraction. Finally, this paper analyzes the influence of different process conditions on internal gradients of catalyst, and concludes the influence of each parameter on effectiveness factor of particle. The increase of temperature, decrease of pressure or increase of LHSV can all cause the decrease of effectiveness factor, wherein the temperature has the most significant effect on the effectiveness factor, followed by LHSV, and pressure has the weakest effect. These findings contribute to a more in-depth understanding of the features and rules of LTCT HDS, and can also give us some guidance for industrial reactor simulation.

1. Introduction

China's energy structure can be summarized as "rich in coal, deficient in crude oil, poor in natural gas", and its dependence on foreign crude oil in 2016 has reached a new high of 65%. The contradiction between oil supply and demand is still one of the key factors restricting China's economic development. Therefore, coal-to-liquids (CTL) technology has become a national strategy and new research hotspot. Up to now, *China Shenhua Coal to Liquid and Chemical Co., Ltd.* 1 million tons/year direct coal liquefaction plant has been put into commercial operation for 7 years, while the 4 million tons/year indirect coal liquefaction demonstration project of *Shenhua Ningxia Coal Industry Group Co., Ltd* has also been completed and put into production in 2016. Besides, as the by-product of *Low Temperature Pyrolysis Process*, LTCT can be hydrotreated to produce clean fuel, which is known as the third path of CTL. Ningdong of Ningxia Provence, Erdos of Inner Mongolia Provence and Yulin of Shaanxi Provence is the core area of energy "Golden Triangle" in China, whose low-rank coal reserves account for more than 55% of the proven coal reserves of the country. With high volatile matter content, low-rank coal is a high-quality raw material for pyrolysis. In that region, the low-rank coal quality-based conversion and utilization industry with pyrolysis as the forerunner has formed a processing capacity of nearly 100 million tons. This industry has become an important development path of coal resources in China in the

* Corresponding authors.
E-mail addresses: lidong@nwu.edu.cn (D. Li), jason@wavenet.cycu.edu.tw (J. Chen).

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Nomenclature

LTCT	low temperature coal tar
HDS	hydrodesulfurization
HDT	hydrotreatment
LHSV	liquid hourly space velocity (h^{-1})
TBR	trickle-bed reactor
CTL	coal-to-liquids
HDN	hydrodenitrogenation
SRGO	straight-run gas oil
HDM	hydrodemetalation
SARA	saturated hydrocarbon, aromatic hydrocarbon, resin and asphaltene
HP	hydroprotecting
DCS	distributed control system
DBT	dibenzothiophene
VGO	vacuum gas oil
DDS	direct desulfurization
HYD	hydrogenation followed desulfurization
n	reaction order of sulfur
m	reaction order of hydrogen
r_{HDS}	chemical reaction rate ($mol\,g^{-1}\,s^{-1}$)
K_{HDS}	reaction rate coefficient
K_0	pre-exponential factor
a	dimensionless number
t_c	catalyst half-life
t_1	running time (h)
EA_{HDS}	activation energy (J/mol)
W_{sul}	mass fractions of sulfur (ppm)
R	universal gas constant
T	temperature (k)
u_g	velocity of the gas ($cm\,s^{-1}$)
$k^L_{H_2}$	gas-liquid mass transfer coefficient for H_2 ($cm\,s^{-1}$)
$k^L_{H_2S}$	gas-liquid mass transfer coefficient for H_2S ($cm\,s^{-1}$)
a_L	specific surface area, gas–liquid interface (cm^{-1})
$P^G_{H_2}$	partial pressure of H_2 (MPa)
$P^G_{H_2S}$	partial pressure of H_2S (MPa)
h_{H2}	Henry's coefficient for H_2 ($MPa\,cm^3\,mol^{-1}$)
h_{H2S}	Henry's coefficient for H_2S ($MPa\,cm^3\,mol^{-1}$)
Z	reactor bed length (cm)
u_l	velocity of the liquid ($cm\,s^{-1}$)
$K^S_{H_2}$	liquid–solid mass transfer coefficient for H_2 ($cm\,s^{-1}$)
$K^S_{H_2S}$	liquid–solid mass transfer coefficient for H_2S ($cm\,s^{-1}$)
K^S_{sul}	liquid–solid mass transfer coefficient for sulfur ($cm\,s^{-1}$)
a_S	specific surface area, liquid–solid interface (cm^{-1})
$C^L_{H_2S}$	concentration of H_2S in the liquid phase ($mol\,cm^{-3}$)
$C^S_{H_2}$	concentration of H_2 in the solid phase ($mol\,cm^{-3}$)
$C^S_{H_2S}$	concentration of H_2S in the solid phase ($mol\,cm^{-3}$)
C^L_{sul}	concentration of sulfur in the liquid phase ($mol\,cm^{-3}$)
$C^L_{H_2}$	concentration of H2 in the liquid phase ($mol\,cm^{-3}$)
C^S_{sul}	concentration of sulfur in the solid phase ($mol\,cm^{-3}$)
L_p	particle size (cm)
Vp	total geometric volume of catalyst (cm^3)
Sp	total geometric external area of catalyst (cm^2)
r_c	radius of cylinder (cm)
N	the number of lobes
L	particle length (cm)
A_1	the lateral area of the geometric shape between lobes (cm^2)
A_2	the common area between each cylinder (cm^2)
d_p	particle diameter (cm)
D_K	Knudsen diffusivity ($cm^2\,s^{-1}$)
D^L_{sul}	molecular diffusivity of sulfur in the liquid ($cm^2\,s^{-1}$)
$D^L_{H_2}$	molecular diffusivity of H_2 in the liquid ($cm^2\,s^{-1}$)
De_{sul}	effective diffusivity of sulfur in the pores of catalyst ($cm^2\,s^{-1}$)
$D^L_{H_2S}$	molecular diffusivity of H_2S in the liquid ($cm^2\,s^{-1}$)
ds	diameter of spherical catalyst particle (cm)
D_R	reactor diameter (cm)
d_c	diameter of catalyst particle (cm)
Lc	length of catalyst particle (cm)
G_L	liquid mass velocity ($g\,cm^{-2}\,s^{-1}$)
T_{meABP}	mean average boiling point (^0R)
Mw	molecular weight ($g\,mol^{-1}$)
t_b	the average molar boiling point (°C)
Kw	Watson's characterization factor
d	the specific density at 20 °C (g/cm^3)
V_{H2}	molar gas volume of H_2 at standard conditions ($NL\,mol^{-1}$)
V_{H2S}	molar gas volume of H_2S at standard conditions ($NL\,mol^{-1}$)
V_p	total geometric volume of catalyst (cm^{-3})

Greek symbols

β	deactivation exponential
α	*LHSV* index
η_{HDS}	catalyst effectiveness factor
θ	particle porosity
τ	tortuosity factor
ρ_P	particle density ($g\,cm^{-3}$)
ρ_b	bulk density of the catalyst particles ($g\,cm^{-3}$)
ε	void fraction of the catalyst bed
ϕ	Thiele Modulus
μ_L	liquid viscosity (mPa·s)
ρ_L	liquid density ($lb\,ft^{-3}$)
v^L_C	critical specific volume of liquid feedstock ($ft^3\,mol^{-1}$)
$v^{H_2}_C$	critical specific volume of H_2 ($cm^3\,mol^{-1}$)
$v^{H_2S}_C$	critical specific volume of H_2S ($cm^3\,mol^{-1}$)
v_L	molar volume of liquid feedstock ($cm^3\,mol^{-1}$)
v_{H_2}	molar volume of H_2 ($cm^3\,mol^{-1}$)
v_{H_2S}	molar volume of H_2S ($cm^3\,mol^{-1}$)
v_{sul}	sulfur molar volume ($cm^3\,mol^{-1}$)
λ_{H2}	solubility coefficient of H_2 ($NL\,kg^{-1}\,MPa^{-1}$)
λ_{H2S}	solubility coefficient of H_2S ($NL\,kg^{-1}\,MPa^{-1}$)
ρ_0	density of tar at 15.6 1C and 101.3 kPa ($lb\,ft^{-3}$)
$\rho_{15.6}$	specific gravity of tar at 15.6 °C
ρ_{20}	density of the tar at 20 °C ($g\,cm^{-3}$)
$\Delta\rho_T$	temperature correction of liquid density ($lb\,ft^{-3}$)
$\Delta\rho_P$	pressure dependence of liquid density ($lb\,ft^{-3}$)

Subscripts

sul	sulfur
H_2	hydrogen
H_2S	hydrogen sulfide
s	solid phase
L	liquid phase
g	gas phase
b	bulk
p	particle

Superscripts

s	solid phase
L	liquid phase
g	gas phase