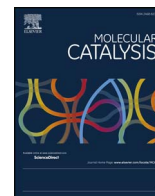




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Mechanistic kinetics and reactor modelling of hydrogen production from the partial oxidation of diesel over a quaternary metal oxide catalyst

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ABSTRACT

The kinetics of the partial oxidation (POX) reforming of diesel was studied using hexadecane as a surrogate for diesel. The kinetic experimental data used were obtained over a 5wt%Ni/Ce_{0.5}Zr_{0.33}Ca_{0.085}Y_{0.085}(5N/CZCaY) catalyst at atmospheric pressure and temperatures of 1123–1223 K in a packed bed reactor. The kinetic model that best described the experimental rates was developed based on the Eley-Rideal (ER) formulation assuming the dissociative adsorption of diesel (hexadecane) on the catalyst active site as the rate determining step. Also, a rate law based reactor model was developed and the resulting partial differential equations solved using finite elements method. A satisfactory agreement between the model prediction and experimental results was obtained which showed that the predicted concentration and temperature profiles for the process justify the assumption of plug flow and isothermal behaviour in the radial direction.

1. Introduction

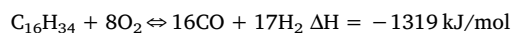
Energy consumption has increased drastically over the past few decades. The transportation and electricity sectors consume a greater share of this energy, which is derived from fossil fuels typically hydrocarbons such as coal, natural gas & crude oil. This has led to a corresponding increase in the emission of pollutants that pose health risks to humans, deplete the ozone layer and have other negative ecological effects. In the past decade, the transportation sector alone has consumed 25% of the world's energy and produced 22% of its CO₂ emissions [1]. As a result, renewable/clean sources of energy have paved the way for research and development towards a sustainable future.

Hydrogen, the most abundant element on earth, constituting 75% of the planet's elemental mass yet does not exist in its elemental form [2], is one of the alternative sources of energy with negligible emission when used as fuel, as the product of its combustion is water vapour. It is mainly produced either from the electrolysis of water or from the reforming of hydrocarbon and is mainly utilized in fuel cell powered vehicles. However, the main obstacle that prevents the use of hydrogen as a fuel currently is the lack of infrastructure and efficient storage technologies [3]. On-board hydrogen production from a suitable liquid source seems to be a more practical short-medium term perspective. Hydrocarbon fuels like kerosene, gasoline, jet fuel and diesel are favoured as the most suitable hydrogen carriers because they are easily transportable and have an existing infrastructure for distribution [4].

However the problem associated with heavy fuels processing is the ease of carbon deposition and soot emission, high temperature at fuel reforming and high energy consumption for fuel evaporation [5].

In this study, the production of hydrogen from diesel fuel is particularly of interest as the key benefits of diesel fuel are its existing worldwide infrastructure, high energy content (about 10 kWh/L), easy handling and the prospect of biomass derived, and therefore carbon neutral biodiesel [6]. This prospect could provide a smooth transition from fossil to renewable feedstock [7]. Partial oxidation (POX) is one of the viable technologies for hydrogen production from diesel fuels which involves the combustion of the fuel at high temperatures in a limited supply of oxygen. POX offers the advantage of lower energy consumption, requires a compact sized reactor to operate and thus suits the on-board application of fuel cells. The challenges however faced with the partial oxidation reforming of liquid fuels is the complex nature of the fuel, the presence of coke precursors that could cause catalyst deactivation, high energy density of the fuel which leads to high temperatures and difficulty in ensuring a homogenous mixture of air and fuel to control combustion and formation of hot spots [4].

With respect to the complex nature of diesel, hexadecane C₁₆H₃₄ is often used as a diesel fuel surrogate as it is the dominant hydrocarbon in certified grade diesel fuel with a composition of about 38.7 wt% [1].



On the other hand, the development of carbon resistant catalysts

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Nomenclature

| | | | |
|--------------|---|-----------------|---|
| A | Area of the reactor | m | Reaction order |
| A_{ij} | Binary interaction parameter | M_{AB} | Average molecular weight of the gas mixture |
| A, i | Hexadecane | $M_{i,j}$ | Molecular weight of pure component |
| B, j | Oxygen | n | Number of components |
| C | Carbon dioxide | N_{Re} | Reynolds number |
| D | Hydrogen | N_{sc} | Schmidt number |
| AAD | Average absolute deviation | N_{pr} | Prandtl number |
| C_i | Concentration of species, kmol/m ³ | N_i | Molar flow rate of species ($i = A, B, C, D$) kmol/s |
| C_v | Concentration of vacant sites | P | Total pressure |
| C_t | Total concentration of active sites on catalyst surface | $-r_i$ | Rate of reaction based on a particular species, ($i = A, B, C, D$) kmol/kgcat.s |
| C_{AS} | Concentration at pellet surface, mol/dm ³ | $-r_{A,obs}$ | Observed rate of reaction, |
| C_{AC} | Concentration at pellet centre, mol/dm ³ | R_C | Catalyst radius |
| $C_{wp,ipd}$ | Weisz–Prater criterion for internal pore diffusion | ΔS | Entropy |
| C_{Ab} | Concentration of A in bulk | T_c | Critical temperature |
| D_{eff} | Effective diffusivity, m ² /s | T | Temperature, K |
| D_{AB} | Bulk diffusivity of component A (hexadecane) in B (oxygen), m ² /s | $T_{bi,j}$ | Normal boiling temperature of pure component i or j , K |
| D_p | Particle size of catalyst | τ | Tortuosity factor, dimensionless |
| ϵ | Void fraction, dimensionless | V_c | Specific volume at critical temperature |
| E | Activation energy, J/mol | v | Average fluid velocity for the mixture, m/s |
| ϵ_i | Characteristic Lennard Jones energy | v_i | Velocity of individual component |
| ΔH | Enthalpy of reaction, kJ/mol | V^*_{i} | Volumetric flow rates |
| ΔH_R | Heat of reaction, KJ/mol | w_i | Mass fraction of component i |
| J_D | Chilton and Colburn J factor | y_i | Mole fraction |
| k_m | Mixture thermal conductivity, W/m K | * | Active surface reaction site |
| k_c | Mass transfer coefficient | λ_{eff} | Effective thermal conductivity, KJ/m.s.K |
| k_i | Thermal conductivity of pure component i at the temperature of interest | σ_{AB} | Characteristic length or average collision diameter, Å |
| k | Boltzmann constant | Ω_D | Diffusion collision integral, dimensionless |
| K_O | Pre-exponential or collision factor | ρ_f | Density of fluid mixture, kg/m ³ |
| K_i | Adsorption constants for the species ($i = A, B, C, D$) | μ_{mix} | Fluid viscosity for the mixture, Pa s |
| K_p | Thermodynamic equilibrium constant | $\mu_{i,j}$ | Vapor viscosity of pure component i or j at the temperature |
| L | Catalyst bed height | \emptyset | Porosity |
| | | ρ_b | Bulk density of catalyst bed given by $(1-\emptyset)\rho_c$ |
| | | ρ_c | Pellet density |

that can withstand deactivation for an extended period of time is required. In line with this, several catalysts have been used in the study of POX of heavy hydrocarbons including pyrochlores [8] and hexa-aluminates [9]. The use of precious metals like Pt, Pd and Rh on oxide supports such as CeO₂, La₂O₃, and ZrO₂ with superior activity and stability have also been reported [10]. Generally, catalysts used for reforming are Ni based because of its lower cost and supported mostly on Al₂O₃, MgO, or other ceramic supports. However, nickel based catalysts are prone to deactivation by coking [11], therefore the development of a robust nickel-based catalyst is important. Innovative support materials, improved Ni dispersion, and use of promoters have been applied to prevent carbon deposition [12], therefore in this study, a quaternary nickel based catalyst containing two metal promoters (Ca and Y) in addition to ceria-zirconia oxide support which yield good nickel dispersion [13], has been used.

Mixture homogeneity is a crucial factor in the design of a reformer, which in turn is dependent on the reaction kinetics, however the kinetics of the partial oxidation reforming of diesel fuels is not widely reported as compared to those of light hydrocarbon fuels like methane [1]. It is therefore pertinent to have an insight into the kinetics of the diesel POX reaction and what takes place in the catalytic packed bed reactor so as to make better predictions that could optimize the performance of the system.

2. Theory

2.1. Kinetic modeling

Developing a kinetic model requires a good expression of the

elementary steps that lead from the feed materials to products. Few reports are available in the literature on the mechanism of this process and have been developed on the basis of the reaction mechanisms and kinetic parameters of the smaller hydrocarbons [14].

The kinetics of hexadecane steam reforming was studied by Patel et al. [1] in which they compared a Power Law model, an Eley–Rideal model, and a Langmuir–Hinshelwood model and estimated the kinetic parameters from experiments in a micro reactor coated with Rh/Al₂O₃ catalyst. While the Langmuir–Hinshelwood model failed mechanistically, and the Power Law model failed to predict the results at high S/C ratios, the Eley–Rideal model reproduced the experimentally measured reaction rates for a wide range of concentrations and temperatures. Thormann et al. [7] also developed a kinetic model and reported an order of 0.5 with respect to hexadecane and activation energy of 71 kJ/mol in their study of the steam reforming of hexadecane over Rh/CeO₂ catalyst. Furthermore, Gawade et al. [1] studied the kinetics of the steam reforming of n-hexadecane and used the first order kinetics power law model, Mars-Van Krevelen model and Eley-Rideal model to fit the experimental data on hexadecane combustion while they used Langmuir Hinshelwood bimolecular model and a Langmuir Hinshelwood dual site model for steam reforming of hexadecane. Consequently, either of the two models did not fit the hexadecane steam reforming reaction mechanism appropriately and the Eley-Rideal model gave a good fit. Other authors have also contributed to the kinetic study of the reforming of diesel [14–16].

Nevertheless, due to the wide variety of catalysts used in the POX reactions carried out by the different authors in literature, it was yet difficult to reach a consensus on a kinetic model for the POX process.

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