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Research article

Numerical simulation of catalytic upgrading of biomass pyrolysis vapours in a FCC riser

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ABSTRACT

Catalytic upgrading of biomass pyrolysis vapours is a potential method for the production of hydrocarbon fuel intermediates. This work attempts to study the catalytic upgrading of pyrolysis vapours in a pilot scale FCC riser in terms of hydrodynamics, residence time distribution (RTD) and chemical reactions by CFD simulation. NREL's Davison Circulating Riser (DCR) reactor was used for this investigation. CFD simulation was performed using 2-D Eulerian–Eulerian method which is computationally less demanding than the alternative Euler-Lagrangian method. First, the hydrodynamic model of the riser reactor was validated with the experimental results. A single study of time-averaged solid volume fraction and pressure drop data was used for the validation. The validated hydrodynamic model was extended to simulate hydrodynamic behaviours and catalyst RTD in the Davison Circulating Riser (DCR) reactor. Furthermore, the effects on catalyst RTD were investigated for optimising catalyst performance by varying gas and catalyst flow rates. Finally, the catalytic upgrading of pyrolysis vapours in the DCR riser was attempted for the first time by coupling CFD model with kinetics. A kinetic model for pyrolysis vapours upgrading using a lumping kinetic approach was implemented to quantify the yields of products. Five lumping components, including aromatic hydrocarbons, coke, non–condensable gas, aqueous fraction, and non–volatile heavy compounds (residue) were considered. It was found that the yield of lumping components obtained from the present kinetic model is very low. Thus, the further research needs to be carried out in the area of the kinetic model development to improve the yield prediction.

1. Introduction

Fast pyrolysis, the rapid heating of biomass in the oxygen–free atmosphere, has been considered as a promising technology for the production of transportation fuels, speciality and fine chemicals, and furnace and boiler fuel [1]. Unfortunately, the produced bio-oil from fast pyrolysis of biomass has a highly complex mixture of oxygenated compounds that considered unsuitable for direct use in existing liquid hydrocarbon fuel technologies such as fractionation units (atmospheric and vacuum distillation), fluid catalytic cracking (FCC), thermal cracking, and hydroprocessing units. The issue thus related to raw pyrolysis bio–oil can be upgraded or treated by catalytic method [2]. Catalytic fast pyrolysis (CFP) has a potential option for improving the quality of organic products from fast pyrolysis of biomass [3]. This process can be operated by either in–situ where the catalyst and biomass are mixed in the same reactor or ex–situ where the vapours from the biomass pyrolysis reactor react with the catalyst in a separate reactor system [4,5]. Ex–situ catalytic fast pyrolysis process or pyrolysis vapours upgrading can be considered a potential method for the production of hydrocarbon fuel intermediates such as carboxylic acids, aldehydes, ketones, furans and phenolic compounds [6]. The chemical reactions occurring in ex–situ catalytic fast pyrolysis include deoxygenation, hydrogen transfer, aromatisation, isomerisation, and C—C coupling reactions [7]. Deoxygenation reaction can be achieved via decarboxylation – removal of oxygen as CO_2, decarbonylation – removal of oxygen as CO, and hydrodeoxygenation – removal of oxygen as H_2O. Hydrogen transfer reaction can occur at atmospheric pressure and at high reaction temperatures without hydrogen [7]. C—C coupling reactions can be achieved via transalkylation (methyl transfer), ketonisation, aldol condensation, and hydroalkylation reactions. Mostly, the ex–situ CFP has been conducted in either micro–scale via Pyro–GC–MS [8–10] or in lab–scale reactor [11–13]. The lab–scale reactor of pyrolysis vapours upgrading was performed in either a fixed bed or fluidised bed reactors. In comparison with fixed bed reactor, fluidised bed operations could be preferred because it produces relatively lesser coke and thus reduces catalyst deactivation [14]. Also, it has the advantages of continuous and quick catalyst regeneration [6]. The pyrolysis vapours upgrading in fluidised bed follows a similar procedure in the

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petroleum industry with the reactor concept of fluid catalytic cracking (FCC). In a typical FCC unit, catalyst from the regenerator enters at the bottom of the riser where it reacts with the feed in the riser and is separated from the gaseous products by the cyclone. The catalyst flows back to the regenerator where the air is injected to burn off the coke that is deposited on the active surface of the catalyst.

In literature, various fundamental studies have already been conducted to understand the underlying mechanism of pyrolysis vapours upgrading and coking process using different microporous catalysts and several process parameters such as feedstock type (pine, red oak, and hybrid poplar) and temperature (400–700 °C) [8–10]. Among the various catalysts tested, HZSM–5 based catalyst is widely applied for the catalytic upgrading of pyrolysis vapours due to its strong acidity, shape selectivity, and ion exchange capacity. However, HZSM–5 deactivates rapidly due to the decrease in its acid sites (Si/Al ratio) [9]. To study catalyst activity during vapours upgrading, Mukarakate et al. [8] have investigated in a horizontal quartz annular flow reactor coupled with a molecular beam mass spectrometer. They have found the deactivation of the catalyst completely at a biomass–to–catalyst ratio of about 3. Wan et al. [9] have investigated the effect of Si/Al ratio and the temperature on the catalytic activity using a CDS analytical pyroprobe with a small packed-bed flow reactor. The reactor has the dimension of 6″ long and ¼″ OD. They have found the higher aromatic yield for HZSM–5 with Si/Al ratio of 40 at 500 °C. Another study has also reported the pyrolysis vapours upgrading in a micro-pyrolyser by investigating the effect of feedstock properties (type: hybrid poplar; size: 0.2–3 mm; and loading: 0.5 mg), and catalyst temperature (400–700 °C) and loading (10–40 mg) [10]. To investigate how the catalyst type influences the vapours upgrading, a lab-scale reactor was also used in the literature. Park et al. [11] have studied the upgrading of pine pyrolysis vapours in a lab–scale fixed catalytic bed reactor using different zeolite catalysts such as HZSM–5, H–Y, and Ga–ZSM–5. They have also investigated the influence of bed temperature, vapours residence time, and catalyst composition on the product distribution. Iliopoulou et al. [15] have reported the catalytic upgrading of pyrolysis vapours in the pilot–scale riser using two different catalysts of FCC catalyst and ZSM–5 based FCC additive catalyst. Though the investigation of pyrolysis vapours cracking has been studied mainly at the lab-scale in the literature, it possesses many challenges at the industrial-scale that need to be addressed. As discussed by Yildiz et al. [16], the challenges include operation mode, life and deactivation of catalyst, and novel process configurations.

The issues related to the cracking of pyrolysis vapours over the catalyst are the lower yield of bio–oil, the higher yield of gas, and high coking rate resulting in rapid deactivation of the catalyst. The formation of coke is mainly from the polymerisation of aromatic hydrocarbon or condensation of unreacted pyrolysis vapours. This is due to low effective H/C ratio of the pyrolysis vapours [8]. The higher yield of gas is due to a heavy fraction of oxygenated compounds in pyrolysis vapours removed as CO_2, CO, and $H_2O(g)$ through decarboxylation, decarbonisation, and hydrodeoxygenation reactions, respectively. Therefore, to retain carbon in the pyrolysis vapours, the reaction pathways involved in the removal of oxygen heteroatom from the pyrolysis vapours need to be optimised [7,14]. Also, the contact time between the catalyst and vapours in the riser need to be optimised [15]. Typical vapours residence time in the fluidised bed riser is to be 2–3 s. However, the longer contact time between catalyst and vapours may form the excessive coking and thus reduce the catalyst activity [8]. The catalyst deactivation due to the deposition of coke on the active surface of catalyst depends on the type of catalyst, reactor configuration, and process conditions. In the view of reactor configuration, it is important to understand the underlying fluid dynamics of the reactor to improve the catalyst performance. Thus, the present study motivates to develop a computational model for the pyrolysis vapours upgrading in the fluidised bed riser. Different modelling approaches have been developed in the literature for studying the hydrodynamics of FCC riser along with reaction kinetic modelling. These approaches are: (i) 1–D hydrodynamic model with lumped kinetics; (ii) 1–D hydrodynamic model with molecular–level kinetics; (iii) 2–D empirical hydrodynamics with the lumping kinetics; (iv) CFD model with the lumping kinetics; and (v) CFD model with molecular–level kinetics [17]. Among them, first three methods are computationally easy to solve with less accuracy, whereas highly detailed information of flow fields and reaction kinetics can be obtained from CFD model with molecular–level kinetics. However, it requires a lot of computational efforts. Most widely used method is CFD with the lumping kinetic modelling, which is more comprehensive and requires a reasonable computational cost with adequate accuracy. In addition, this method has been applied to the crude oil cracking in the FCC riser [18,19] and fast pyrolysis of biomass for biofuel production [20–22].

The present work aims to simulate the hydrodynamics of pyrolysis vapours and catalyst in a Davison Circulating Riser. The Davison Circulating Riser (DCR) is the industry standard FCC pilot–scale reactor developed by Grace's [23]. The National Renewable Energy Laboratory (NREL) has recently studied biomass pyrolysis vapours upgrading using the Davison Circulating Riser (DCR) [12,24]. In which, the vapours were fed to continuously circulating catalyst for hydrocarbon production without adding hydrogen. It has advantages of continuous coke removal to keep the catalyst in the active form. In this work, the hydrodynamic characteristics of pyrolysis vapours and HZSM-5 catalyst in the riser are calculated using 2-D Eulerian–Eulerian approach. Using hydrodynamic results, the prediction of catalyst residence time in the riser is performed for studying the contact time of vapours with the catalyst. This is examined by the effect of catalyst feed rate and gas flow rate on the hydrodynamic behaviour and catalyst residence time distribution (RTD). Furthermore, the hydrodynamic model is extended to simulate the catalytic upgrading of pyrolysis vapours by a coupled CFD–lumping (pseudo–components model) kinetic approach. Five lumps of the major products in pyrolysis upgrading, including aromatic hydrocarbons, coke, non–condensable gas, aqueous fraction, and non–volatile heavy compounds (residue) are considered.

The rest of the paper is organised as follows. Section 2 describes the modelling approaches with governing equations used for predicting the flow fields in the riser and Section 3 describes the numerical methodology and solution algorithm implemented in this study. The results obtained from this study are discussed in Section 4. The conclusions drawn from this numerical study are presented in the final section of the paper.

2. CFD modelling

Ensemble averaged conservation equations of mass, momentum, and energy were used to describe the flow fields of catalyst and pyrolysis vapours in the riser. All phases are described as interpenetrating continua in an Eulerian frame of reference. Gas phase is treated as a continuous phase which consists of pyrolysis vapours and nitrogen. It is worth to mention that aerosol is also formed during the pyrolysis process and is carried through together with vapours. However, it is not included in the gas phase mixture to avoid the complexity of the model. A catalyst particle is considered as the dispersed solid phase.

2.1. Hydrodynamic equations

The continuity equation for gas (g) and particle phases (p) can be written as [25]

$$\frac{\partial}{\partial t}(\alpha_g\rho_g) + \nabla\bullet(\alpha_g\rho_g\vec{v_g}) = S_g \tag{1}$$

$$\frac{\partial}{\partial t}(\alpha_p\rho_p) + \nabla\bullet(\alpha_p\rho_p\vec{v_p}) = S_p \tag{2}$$

where ρ, α, and $\vec{v}$ are the density, the volume fraction and the