Numerical Study on Catalytic Hydrodeoxygenation of Pyrolytic Bio-Oil Model Compound, Guaiacol, in Fluidized Bed Reactor

By

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Abstract

The bio-oil obtained by thermochemical conversion of lignocellulosic biomass consist of large fractions of oxygenated compounds which deteriorate its quality leading to low calorific value, high viscosity, high density, high moisture content, etc. Therefore, the bio-oil should be deoxygenated using hydrogen in the presence of appropriate catalyst to improve its properties. Adequate literature on pyrolysis of biomass within the framework of computational fluid dynamics is available but only a couple of papers available on hydrodeoxygenation of bio-oil obtained by pyrolysis. Thus, in this study, guaiacol has been selected as a representative model compound of phenolic fraction of bio-oil for upgrading it by catalytic hydrodeoxygenation. The reaction process has been implemented in a fluidised bed reactor in the presence of palladium catalyst, Pd/Al₂O₃ using computational fluid dynamics (CFD) based solver, ANSYS Fluent 14.5. The range of conditions considered herein are: weight-hourly space velocity (WHSV) = 1, 3 and 5 h⁻¹; superficial H₂-gas velocity, u = 0.075, 0.15 and 0.25 m/s; catalyst load = 0.06 kg and temperature, T = 548 K, 573 K, and 598 K. The solver has been thoroughly validated in terms of grid dependence study, time step size dependence study validating hydrodynamics and HDO results wherever possible with existing literature results. The HDO of guaiacol produces phenol as the most abundant compound along with significant amount of cyclopentanone and methanol. The formation of cyclopentanone from HDO of guaiacol is favourable at high temperature whereas low temperature conditions favour formation of methanol and phenol.

Keywords: Bio-oil; Hydrodeoxygenation; Guaiacol; CFD; Phenol; Catechol; Cyclopentanone; Methanol
1. Introduction

Broadly speaking many sectors in the world today depend on energy sector as a major impetus upon which majority of their activities coordinate. The transport sector being the leading one and is estimated to consume approximately one-fifth of the total produced global energy [1]. This rate however, is likely to accelerate even further due to population growth, improved standards of living and the drive for economic growth by many developing economies. The non-renewable conventional fossil fuels (oil, gas and coal) are the most dependable global energy resources. Oil is the leading one and accounts for one-third of the global energy consumption [2]. Although it is economically viable to extract energy from fossil fuels compared to renewable energy resources, fossil fuels are detrimental to the environment through greenhouse gases emission especially CO₂. Fossil fuels are non-renewable thus high dependence on them may result into depletion albeit new conventional reserve discoveries and improved technologies currently available to extract fossil fuels even from tight non-conventional reserves. Because of above-mentioned factors and among others there is relentless shift in attention towards cleaner and lower carbon alternative or renewable energy resources that are environment friendly. Statistical review carried out by British Petroleum, BP in 2017 [2], shows that renewable energy including biofuels despite having the least share of 4% was the fastest growing energy accounting almost a third of increase in primary energy. Similarly, according to BP energy outlook 2030 [3] it is estimated that renewable energy will contribute 17% increase in global energy supply by the year 2030. Therefore, the future for global energy is renewable resources with bio-oil obtained from biomass-waste being the most promising alternative fuel to petroleum fuels.

There are several approaches available to convert biomass into bio-energy out of which thermochemical conversion methods have wide acceptance [4, 5]. The processes such as gasification, combustion, pyrolysis and liquefaction fall under thermochemical conversion processes. Pyrolysis method has been extensively researched in order to produce bio-oil from lignocellulosic waste biomass. However, the bio-oil obtained by pyrolysis suffer from severe drawbacks such as low calorific value, high density, high viscosity, high moisture content, low pH, etc. This is mainly due to presence of large fractions of oxygenated compounds. Thus by removing these oxygen-fraction, the quality of bio-oil improves in terms of calorific value, density, viscosity, moisture content, etc. much close to the quality commercial gasoline, diesel and kerosene range fractions. Catalytic hydrodeoxygenation is one of the most appropriate approach
to remove oxygenated fractions from the compounds of bio-oil using hydrogen in the presence of an appropriate catalyst. Furthermore, with advancement in computation, CFD has extensively been used in modelling, design, predicting, optimization and improving a number of chemical processes while reducing costs associated with experiments and other unclassified expenditures. A legion of researchers has used CFD successfully to study hydrodynamics as well as chemical conversions of processes involving biomass pyrolysis, gasification, coal combustion and fluid catalytic cracking. In the recent past, a couple of studies have also used CFD for modelling and simulations of hydrodeoxygenation of bio-oil model compounds using lumped kinetic parameters so that to gain insight into the processes and to provide scale-up solutions [6, 7]. Therefore, in this study, a model compound of phenolic fraction of bio-oil, guaiacol, has been considered to study its hydrodeoxygenation behaviour in a fluidized bed reactor. Wide range of conditions have been chosen namely: weight-hourly space velocity (WHSV) = 1, 3 and 5 h⁻¹; superficial H₂-gas velocity, u = 0.075, 0.15 and 0.25 m/s; catalyst load = 0.06 kg and temperature, T = 548 K, 573K and 598 K.

2. Literature Review

The literature on CFD modelling and simulation of hydrodeoxygenation of bio-oil is limited to recent studies of Subramanyam et al. [6] and Gollakota et al. [7]; hence literature pertaining to CFD applied to pyrolysis, gasification, combustion, fluid catalytic cracking, etc. are presented herein. In an attempt to explore and improve computation research carried out in modelling thermochemical conversion of biomass, C.Di Blasi [8] reviewed numerous previous reports in state of the art modelling of biomass pyrolysis. The author described chemical kinetics, activation energy models as well as different approaches used in particle transportation models. Nonetheless, the author cited need for more experimental data to validate models of different reactors. Bruchmu¨ller et al. [9] presented a DEM/CFD 3-D model using an Eulerian/ Lagrangian approach to study thermochemical degradation process of biomass inside an experimental 100 g/h lab scale bubbling fluidised bed reactor. Thorough analysis of the 3-D simulations indicated that fast pyrolysis of biomass to yield bio-oil is vast influenced by local flow of the biomass influenced by the superficial fluidisation velocity rather than the particle such properties as moisture content. Xue et al. [10] developed an Euler-Euler CFD computation model coupling pyrolysis of biomass particles with multi-fluid hydrodynamics model for gas-particle flow. The author to study biomass
pyrolysis process in a fluidized bed reactor implemented this model. Experimental validation of the model with data demonstrated accurate qualitative and quantitative capability to describe complex conversion of biomass and transport processes. Similarly, Ranganathan and Gu [11] carried out CFD modelling of biomass fast pyrolysis using the same reactor as Xue et al [10]. The author first studied hydrodynamics of the reactor and later investigated different kinetic schemes for fast pyrolysis of biomass of different particle density and size at various gas velocity.

Papadikis et al. [12] investigated and compared two cases involving 2-D and 3-D geometry approaches for modelling momentum transport in a 150 g/h lab scale fluidised bed reactor. The author obtained different results based on the different geometry approaches. However, due to computation limitations exhibited by 3-D geometry the author generally recommended 2-D geometry for research purposes. Nevertheless, Papadikis et al. [13] continued the same research modelling fluid-particle interaction in the same reactor further incorporating reaction kinetics of biomass with the properties of the moving discrete particle of the biomass. The author investigated the effect of heat and mass transport of the fluidising gas and reported that the model predicted residence time of the vapours and the particles. Mellin et al. [14] carried out CFD modelling of biomass pyrolysis incorporating a complex reaction scheme including formation of components such as levoglucosan. Results predicted that pyrolysis products reflected the experimental yield satisfactorily. Similarly, the author noted complete conversion of hemicellulose than cellulose and lignin. Lee et al. [15] analysed the effect of reaction temperature on reaction rate and final product yield using two simulation models viz lumped model and hybrid model. It was noted the yield of tar from the hybrid model prediction was consistent with experimental results than the lumped model. However, for char yield both model results obtained from simulation were close to those from the experiment.

The hydrodynamic behaviour of a fluidised bed reactor is an important parameter towards effective thermochemical degradation of biomass. Hydrodynamics determine the rate of elutriation of the solid phase and ultimately chemical reaction. Parametric studies by Xiong et al. [16] on the effect of bubbling hydrodynamics on temporal variations in the exit tar yield for biomass pyrolysis predicted that increasing the fluidisation velocity increases temporal variations in the tar yield. The author carried out this research using computational study of an experimental lab scale reactor and further noted that increase in the diameter of sand particles decreases the yield of tar while the reverse is true to the mean tar yield with increasing the initial sand bed height. Different from
Xiong et al. [16], Min et al. [17] carried out experiment investigation to validate CFD simulation results of a lab-scale fluidised bed reactor in order to determine the extent CFD models capture experimental observation of gas hold up distribution. The author reported agreement of experimental observations with the CFD model. However, generally CFD simulations implementing Syamlal-O’Brian and Gidaspow drag models yield good prediction compared to experimental data. Although fluidised bed reactors have wide application in thermochemical conversion processes of biomass, research using other types of reactors has accordingly been carried out. For instance Choi et al. [18] carried a numerical study of woody biomass conversion. The author reported secondary tar generation along the down-stream of the flow near the inlet of the reactor and further noted increase in granular temperature due to granular acceleration of the solid particles toward the downstream flow.

Nevertheless, computational research involving CFD modelling and simulation of thermochemical processes has also been extended beyond biomass pyrolysis to other processes such as coal combustion and gasification. Earlier work done by Fletcher et al. [19] developed a detailed computational fluid dynamics (CFD) model based on CFX package to simulate flow and reaction in an entrained flow biomass gasifier. According to the author, the simulations results from the model indicated significant difference between using Reynolds stress model and k-ε model for non-combusting case compared to the reacting case. Williams et al. [20] modelled coal combustion presenting correlations for predicting the initial char surface area, porosity and pore structure evolution during char burnout. Similarly, Backreedy et al. [21] developed CFD–based coal and char combustion models to predict the effect of coal maceral content on combustion process. The models incorporated swelling and variable surface area, annealing and ash effects. Sensitivity checks by the author indicated that calculation of the unburned carbon in ash depends on the correct choice of the reaction and physical parameters. Similarly, Yu et al. [22] developed a comprehensive Two-fluid model to simulate coal gasification in a bubbling fluidised bed reactor to predict the impact of flow behaviour on chemical reactions. Simulation results from the model predicted better flow behaviours of the gas and solid phases in the bed and free board of the reactor compared to experiments. The author further noted reasonable change in trend of gas composition profile along the gasifier.

Bhuiyan et al. [23] modelled co-combustion of coal and biomass firing under air and oxy-fuel conditions in small scale furnace. The author varied the mass of biomass input to the total fuel
contribution and noted no increase in CO₂ concentration with increase of biomass contribution proving that biomass is a CO₂–neutral source of energy. Torresi et al. [24] simulated combustion of pulverised coal in an industrial burner. Numerical analysis of the results confirmed excellent burner performance. Recently, Madejski and Modliński [25] also carried out a numerical investigation on combustion of pulverized coal in an industrial power plant boiler using two CFD codes. Analysis of the behaviour of flow of pulverised coal through the burner as well as temperature and velocity distribution agreed with simulation results. Although much focus has been directed toward boiler simulation at nominal load, the author concluded that it is possible to perform numerical studies of coal combustion at different boiler loads.

Notwithstanding the application of CFD in the study of the above processes it also has been applied in hydrodynamic analysis and study of fluidised catalytic cracking (FCC) reactions. Soundararajan et al. [26] modelled methanol to olefin process in a fluidised bed reactor at 450 °C and atmospheric pressure. Modelling studies by the author showed that selectivity towards ethylene increased significantly with increase in coke deposit on the catalyst. However, higher amount of coke deposition on the catalyst beyond 5 wt% inhibits the increase in ethylene yield. Similarly, Zhuang et al. [27] simulated coke deposition and distribution during methanol to olefin reaction as a function of feed temperature, feed composition and space velocity over SAPO-34 catalyst in a fixed bed reactor. It was noted higher feed temperature could promote methanol conversion and accelerate catalyst deactivation. Chang et al. [28] investigated on hydrodynamics and kinetic reactions in a fluidised bed methanol to olefin reactor. Results from simulation indicated that the rate of conversion of methanol and product yields are more sensitive to reaction and pressure than initial methanol content in the feedstock.

Behjat et al. [29] developed a 3-D CFD model of a reactor to study cracking reactions, hydrodynamics, heat and mass transfer of a three phase (gas-liquid-solid) six-lump reaction scheme. The author further investigated the evaporation tendency of the feed droplets into a gas-solid flow. It was found evaporation of gas oil droplets and cracking reactions have profound effect on gas-solid flow and temperature. Similarly, Chang et al. [30] used CFD to study hydrodynamics and cracking reactions in a heavy oil riser. The author reported that product yields are more sensitive to injection angle into the riser than droplet size of the feedstock and reaction temperature. Nonetheless, Yang et al. [31] developed a three-dimensional model to investigate hydrodynamics, heat transfer and cracking reaction to maximise propylene production.
implementing an 11-lump kinetic model. The author analysed effects of injecting angle of the nozzle on flow and thermal patterns at the feed injection zone. It was recommended wider angles of injection induce high radial velocities, better heat transfer and desirable reaction performance. Recently, Pelissari et al. [32] also simulated the hydrodynamics, heat transfer and heterogeneous catalytic cracking reactions within a riser using a 12-lump kinetic model. The author proposed a catalyst deactivation model dependent on the weight percentage of coke amount on the catalyst. Analysis of results indicate treatment for coke has significant role in simulation with catalyst deactivation as a function of coke amount on catalyst.

Finally, based on the aforementioned literature survey, it is clear that much emphasis has been focused on CFD applied to biomass pyrolysis, coal combustion, gasification and fluid catalytic cracking. However, CFD applied to hydrodeoxygenation of bio-oil has received negligible attention except those of Subramanyam et al. [6] and Gollakota et al. [7]. Thus, HDO of bio-oil has been carried out using a representative bio-oil model compound of phenolic group, guaiacol. The reaction has been implemented in a fluidised bed reactor using palladium catalyst objectively to study the effect of temperature, weight hourly space velocity and superficial velocity of hydrogen gas.

3. Problem Statement, HDO Kinetics and Mathematical Formulation
The schematic illustration of a fluidized bed reactor used for the hydrodeoxygenation of guaiacol is shown in Figure 1 which is of height (H) 1.0m and diameter (d) 0.28m. The reactor is packed up to an initial packing height (H₀) of 0.4m corresponding to solids volume fraction of 0.6. Authors have chosen this size of reactor for the validation purpose (without hydrodeoxygenation reaction) with the study of Taghipour et al. [33] who have reported experimental and computational results on fluidization behaviour of glass beads as solid particles of size 275µm and density 2500kg/m³. The validation part is shown in a subsequent section. For the case of HDO of guaiacol, the same reactor size having same initial packing bed height, size of packing material and solid bed volume fraction as in the case of Taghipour et al. [33] has been used. However, the packing material type is now mixed Pd/Al₂O₃ catalysts and glass beads while the fluidized medium is hydrogen gas along with the bio-oil model compound, guaiacol. Alternatively, it can be said that the hydrogen gas and guaiacol are introduced in to the reactor at different flow rates where the guaiacol flow rate is computed depending on calculated based on the required value of the weight hourly space velocity.
The temperature inside the reactor is maintained constant for a given run and three different temperatures are considered for which kinetics of guaiacol HDO are available due to experimental work of Gao et al. [34]. For specified hydrogen gas superficial velocity, reactor temperature and bio-oil mass flowrate per unit mass of catalyst (i.e., WHSV) and corresponding kinetics at that temperature, different degree of HDO of guaiacol take place inside the reactor producing phenol, catechol, cyclopentanone, methanol, water and gases which occupy the freeboard of the reactor in addition to interstitial spaces between the catalyst particles. The performance of HDO would strongly be affected with the distribution of solids in the reactor while fluidization is occurring in addition to momentum and heat transfer amongst three different phases. Thus, species involved in this study are grouped into three phase mixtures, i.e., bio-oil phase mixture, gas-phase mixture and solid-phase mixture. The thermo-physical properties of these phases can be in Table 1. The bio-oil mass flow rate into the reactor is determined based on the value of weight hour space velocity. Flow conditions of both bio-oil model compound and hydrogen gas superficial velocity used in this study are summarized in Table 2. The catalyst’s volume fraction inside the reactor is very small (only 0.0002) compared to the volume of the reactor. Thus, in order to make the bed height of up to 0.4m as well as increase the solids bed density in the present HDO reactor, glass beads of the same size and density same as used in the study of Taghipour et al. [33] was added to the catalyst bed. The solids volume fraction $\alpha_s$ inside the reactor was determined by expression $\alpha_s = \frac{W_s}{\rho_s A H_0}$ where, mass of solid particles, $W_s$ (= wt. of catalyst + wt. of glass beads) and density of solid particles is $\rho_s$; $A$, represents the cross-section area of the reactor and $H_0$, the bed height of packed solid particles. Density of solids mixture was calculated using the mixing law $\rho_s = \frac{1}{\sum_i \left(\frac{y_i}{\rho_i}\right)}$ where $\rho_i$ represents density; $y_i$, mass fraction of each species “i” in the solid’s mixture. Finally, the reaction kinetics are adopted from the work of Gao et al [34] who carried out an experimental investigation on HDO of guaiacol and proposed five reaction pathways. The main products of the reactions include phenol (PHE), catechol (CAT), and cyclopentanone (CYC). Other products include methanol (MeOH), water and gases. The reaction kinetic parameters of HDO of guaiacol in terms of activation energy $E_{a,i}$ and pre-exponential factors $A_i$ are shown in Table 3.

The governing equations of the combined fluid flow, heat transfer and chemical reactions occurring during HDO of guaiacol in the fluidized bed reactor namely conservation of mass (continuity equation), momentum, energy due to heat transfer, transport of chemical species and
other constitutive equations derived from kinetic theory of granular flow are standard in the
domain of computational fluid dynamics hence are provided in the electronic supplementary
information (ESI).

4. Numerical Methodology

Two-dimensional (2-D) reactor geometry of height 1.0 m and diameter 0.28m created and meshed
using computer-aided design software (CAD) in the ANSYS 14.5 workbench. The geometry
meshed to create high quality regular grids using equal radial and axial grid interval spacing. The
boundaries specified are one inlet, one outlet and two stationary walls. To ensure accuracy,
convergence and increase speed of the numerical solution, the grid varied from coarse to fine and
finest by altering the grid interval spacing in the order 0.005m, 0.002m and 0.001m, which
corresponds to 11200, 70000 and 157500 cell elements respectively. The grid sensitivity analysis
carried out for the case of hydrodynamics modelling to investigate the effect of grid size on the
numerical results. Results obtained did not show appreciable variation although computation time
increased as the number of cell elements increased. To reduce computation cost of and still obtain
mesh independent results, a fine mesh (consisting of 70000 cell elements in the entire reactor
geometry) selected to investigate reaction kinetics.

ANSYS FLUENT 14.5 commercial CFD solver used to simulate transport and variation of
species concentration due to chemical reaction based on multiphase Eulerian model. All pertinent
equations for this simulation work are provided in electronic supplementary information (ESI) of
this work. In order to model transport of species, thermo-physical properties of species that are not
available in the fluent database are manually added to the solver. The species mixed and lumped
into three different phase mixtures, i.e., gas-phase mixture, oil-phase mixture and solid-phase
mixture. The gas-phase mixture has been chosen as the most abundant and primary phase while
oil-phase and solid-phase mixtures have been considered secondary phases. The average
properties of the mixture evaluated by properties of each fluid phase that are involved in the
mixture. The thermal conductivity and viscosity of the oil phase mixture calculated by the mass-
weighted mixing law. The density of the oil–phase and gas–phase mixtures evaluated using
incompressible ideal gas law. Similarly, solid-phase mixture density computed by the volume-
weighted mixing law. The reaction was assumed to occur only between species of different phase
mixtures. In other words, species in the same phase mixture are independent and do not react. The
heterogeneous stiff chemistry solver implementing the finite-rate eddy dissipation model to facilitate convergence has solved the interphase heterogeneous reactions. All reactions in the solver implemented on the volume basis. The values of pre-exponential factors, activation energy, and rate exponent and stoichiometry coefficients of the chemical reactions also specified. The rate of reaction has been determined using Arrhenius kinetic expression. The Schiller and Naumann [35] drag function has been used to represent interphase momentum transfer between fluid–fluid interaction whereas the fluid–solid momentum transfer interactions has been solved accordingly by using Gidaspow [36] drag function. The restitution coefficient set to 0.9. The Ranz-Marshall [39] expression of heat transfer coefficient has been used to compute the volumetric rate of energy transfer in the reactor between the oil-phase and gas-phase mixtures. Similarly, Ergun [38] expression for the energy transfer between the solid-phase and the gas-phase mixtures has been selected.

Appropriate conditions at the boundaries have been selected to obtain a steady numerical solution. To permit flow into the reactor, the velocity-inlet boundary condition has been specified at the inlet of reactor. The feed consisting of gas and bio-oil feed enters the reactor and flows upwards together under fluidization conditions of velocity determined from weight hourly space velocity (WHSV); and the velocity kept constant throughout the reaction time. The boundary condition at outlet of the reactor set to pressure outlet and the value of pressure at the outlet was specified 101325 Pa. At the walls of reactor, a no-slip boundary condition specified. Across all boundaries, the flow conditions, composition of the species in terms of mass fraction, multiphase volume fraction and thermal boundary conditions have specified for each phase depending on the operating conditions and maintained constant for entire reaction time.

Governing equations (please see ESI) have been solved by ANSYS FLUENT 14.5 using a pressure based-solver employing finite volume method and a PC-SIMPLE algorithm for pressure-velocity coupling in transient time. Turbulence due to random mixing of the phases resulting from fluidization was implemented using k-ε model with enhanced standard wall treatment. Further, the first order upwind scheme used to discretize convective terms of the governing equations and the solution initialized from all zones of the domain. It was however assumed that at time t = 0s only the solid-phase was present in the reactor i.e., before the bio-oil and hydrogen gas flows into the reactor. Thus, volume fraction of the oil-phase and gas-phase mixtures in the reactor before
solution initialization is zero. A specific region was adopted in the reactor to patch the solid-phase binary mixture (glass beads and Pd/Al₂O₃ catalyst) with values \( X_{\text{max}} = 0.28 \text{m} \) and \( Y_{\text{max}} = 0.4 \text{m} \) coordinates of the region corresponding to diameter of reactor and initial static bed height, \( H_0 \), of the solids phase. The volume fractions of the solid phase mixture and oil-phase and gas-phase mixtures calculated from operating conditions each specified and patched. A time step size of 0.001s and 20 iterations per time step for 10000-time steps chosen after appropriate time-step sensitivity test carried out as reported in the subsequent section. An absolute convergence criterion of 0.001 used to monitor residuals of the solution between successive iterations. The results of the numerical solution exported and processed using CFD post processor to delineate effect of various combinations of WHSV, temperature and superficial velocity.

5. Results and Discussion

5.1. Effect of grid size, time step and validation

Literature results by Taghipour et al. [33] was used to validate the hydrodynamics of a non-reacting gas-solid fluidized bed system by maintaining identical conditions, i.e., using air as fluidizing medium. The other identical conditions include that the reactor was packed with solids (glass beads) of density 2500 kg/m³ and mean diameter of 275µm to an initial static bed height \( H_0 = 0.4 \text{m} \) corresponding to solids volume fraction 0.6. In other words, the study of Taghipour et al. [33] replicated here for the purpose of validation. Then in the later course (as discussed in subsequent subsections of results), the HDO reaction of guaiacol is incorporated using hydrogen gas and bio-oil model compound as fluidizing medium with the bed being made up of both catalysts and glass beads as discussed in preceding section on problem statement.

The effect of variation in grid and validity in terms of bed expansion ratio with the existing experimental and numerical literature results [33] by using different types of drag models displayed in Figures 2. To be specific, Figure 2 display effects of mesh, different drag models and comparison of bed expansion ratio with their experimental and numerical literature counterparts. The corresponding bed expansion ratio (i.e., the ultimate height (H) of the fluidised bed relative to the static height (\( H_0 \)) of the packed bed) of solids in the reactor (as shown in Figure 2) using various drag models indicate that increasing fluidisation velocity reduces particle weight and resistance.
favouring more particle elutriation and bed expansion. Drag models of Wen-Yu, Syamlal and Gidaspow give good description of fluidisation. However, Wen-Yu drag model depicts no bed expansion at minimum fluidisation velocities. Nevertheless, Syamlal drag model shows much prediction of fluidisation at higher velocity. Although there are some deviation perhaps due to variation in mesh, qualitatively the present results are consistent with results obtained by Taghipour et al [33] as shown in Figure 2.

Figure 3 displays combined effects of grid size, time step and drag models on time averaged bed height at air superficial velocity of u = 0.38m/s. It can be noted from Figure 3 that after approximately t =2.0s, the height of the fluidised bed relatively remains constant for the rest of the time. Similarly, at various grid size and time step size (TS), the Gidaspow drag model predicts high solids bed fluidisation and relatively better constant hydrodynamic stability hence solids volume fraction compared to Syamlal drag model. There is less disparity in results from those reported in literature by changing the mesh grid and time step sizes respectively. In fact, there is 5% calculated error in bed expansion due to varying the latter parameters. This shows results obtained during gas-solid fluidisation are independent of the variation in the size of the mesh as well as the time step size for both drag models of Gidaspow and Syamlal. Since Gidaspow drag model is the most used model to describe dense fluidised beds, therefore it is selected for rest of the simulations where HDO is also incorporated. Similarly, to reduce computation time, the step size of 0.001s and a fine mesh chosen.

5.2. HDO of Guaiacol

Figure 4 indicates the distribution of methanol, phenol, cyclopentanone and catechol in the product mixture of guaiacol hydrodeoxygenation at low superficial H₂-gas velocity (u=0.075 m/s) of hydrogen gas. It can be noted from Figure 4 that increasing WHSV or guaiacol flow rate has less significance on distribution of methanol, cyclopentanone and phenol in the product mixture. There is a consistent relationship observed between mass fraction of methanol and phenol. It can be observed that at various WHSV, mass fraction of the two compounds decreases with in temperature increase from 548 K to 598 K. However, different from phenol and methanol, mass fraction of cyclopentanone in the mixture increases with increase in temperature. The typical percentage variation in mass fraction of phenol, cyclopentanone and methanol obtained at each constant WHSV for extreme temperatures is 13%, 50% and 30% respectively. Much as phenol
depicts higher fraction in the mixture, phenol shows least percentage increase compared to methanol and cyclopentanone. This analysis indicates that formation of cyclopentanone from HDO of guaiacol is favourable at high temperature whereas methanol and phenol are more favourable at low temperature conditions.

Unlike the other three compounds, formation of catechol in the mixture depends on WHSV and varies differently at various temperatures. It can be seen at T=548 K and T=573 K, catechol accordingly exhibits high and low mass fraction at WHSV=1 h\(^{-1}\) (guaiacol flow rate). However, as WHSV increases mass fraction of catechol at T=573 K increases steadily while at T=548 K decreases with minimum fraction of the compound depicted at WHSV=3 h\(^{-1}\). A consistent similar observation at T=548 K is also seen at T=598 K. Although catechol fraction in the mixture increases with guaiacol flow rate, generally the compound has uniformly very low or none fraction compared to other HDO products of guaiacol. Comparing results obtained at another H\(_2\)-gas superficial velocity, Figure 5 shows that product distribution of guaiacol HDO for instance at \(u=0.25\) m/s is somewhat analogous to \(u=0.075\) m/s notwithstanding disparity in results of mass fraction of catechol. In fact at \(u=0.25\) m/s catechol formation in the mixture occurs only at moderate temperature T=573 K.

By varying H\(_2\)-gas velocity at T= 548 K as indicated in Figure 6, both methanol and phenol exhibit a consistent pattern in variation of mass fraction opposite to cyclopentanone. It is typically observed that as H\(_2\)-gas velocity progressively increases from 0.075 to 0.25 m/s methanol fraction at WHSV (= 1 h\(^{-1}\)) decreases and at WHSV=5 h\(^{-1}\) increases with an equal percentage of 0.12 %. Similar observation is depicted with phenol however, with a corresponding factor of 0.04 %. Generally high H\(_2\)-gas superficial velocity (\(u=0.25\) m/s) favours formation of methanol and phenol at low WHSV and favours cyclopentanone formation at high WHSV (=5 h\(^{-1}\)). Catechol shows corresponding decrease and increase in mass fraction but at WHSV= 1 and WHSV=3h\(^{-1}\) respectively as H\(_2\)-gas velocity increases.

At T=598K, increasing H\(_2\)-gas superficial velocity shows that mass fraction of cyclopentanone and phenol exhibit uniform distribution in mass fraction at various WHSV. It is observed that as H\(_2\)-velocity increases from \(u= 0.075\) to \(u=0.25\) m/s there is progressive uniform decrease and increase in mass fraction of cyclopentanone whereas phenol shows a uniform increase and decrease pattern. Although at high H\(_2\)-gas velocity (\(u=0.25\) m/s) progressive increase
in guaiacol flow rate (WHSV) increases formation of cyclopentanone. Typically to note from Figure 7 is that low H2-gas velocity (u=0.075 m/s) favours high formation of cyclopentanone at both moderate and high guaiacol flow rates. Catechol shows similar pattern as cyclopentanone however, high mass fraction of catechol in the product mixture is attained at moderate WHSV=3 h⁻¹. Like at T=548 K in Figure 6, methanol and phenol show similar pattern of formation at WHSV=1 h⁻¹ and WHSV=5h⁻¹ as H2-gas velocity increases. Generally, at T=598 K, low H2-gas velocity (u=0.075 m/s) and high guaiacol flow rate is suitable for formation of cyclopentanone whereas phenol formation is more favourable at moderate velocity of H2-gas (u=0.15 m/s) and low guaiacol flow rate. Similarly, high fraction of methanol and catechol corresponds to high H2-gas velocity and moderate guaiacol flow rate (WHSV= 3h⁻¹). Figures 8(a) and 8(b) shows the reaction progress of guaiacol HDO. Guaiacol undergoes conversion yielding significant amount of phenol, cyclopentanone and methanol with approximate percentage fractions of 60%, 25% and 15% respectively. There is very little or no catechol formed. Hydrodeoxygenation of guaiacol produces a range of products. From the reaction progress it can be said guaiacol HDO proceeds via direct demethoxylation to phenol with subsequent formation of methanol and direct hydrogenation forming cyclopentanone as proposed by Gao et al. [34].

Conclusions

The hydrodeoxygenation of guaiacol has been carried out in a fluidized bed reactor within the framework of computational fluid dynamics over wide ranges of hydrogen superficial velocity, weight hourly space velocity and temperature. The fluidization behaviour has been validated with the existing literature results in the absence of HDO. The hydrodeoxygenation of guaiacol produces phenol as most abundant product (60%) and significant amount of cyclopentanone and methanol with approximate percentage fractions of 25% and 15% respectively. There is very little or no catechol formed. At T=598 K, low H2-gas velocity (u=0.075 m/s) and high guaiacol flow rate is suitable for formation of cyclopentanone whereas phenol formation is more favourable at moderate velocity of H2-gas (u=0.15 m/s) and low guaiacol flow rate. Similarly, high fraction of methanol is formed to high H2-gas velocity and moderate guaiacol flow rate (WHSV= 3h⁻¹). At T=548 K, high H2-gas superficial velocity (u=0.25 m/s) favours formation of methanol and phenol at low WHSV (WHSV=1h⁻¹) and favours cyclopentanone formation at high WHSV (=5 h⁻¹). In
general conclusion formation of cyclopentanone from HDO of guaiacol is favourable at high temperature whereas methanol and phenol are more favourable at low temperature conditions.

**Nomenclature**

**Subscripts**

- \( l \) fluid phase
- \( s \) solid phase
- \( q \) phase (gas phase, liquid phase or solid phase)

**Abbreviations**

- WHSV weight hourly space velocity, \( h^{-1} \)
- \( E_a \) activation energy, \( J/kg-mol \)
- HDO Hydrodeoxygenation
- CFD computational fluid dynamics
- \( \text{Pd/Al}_2\text{O}_3 \) palladium catalyst on alumina support
- \( \text{CO}_2 \) carbon dioxide
- \( \text{O} \) Oxygen
- \( \text{CO} \) carbon monoxide
- \( \text{H}_2 \) hydrogen
- \( \text{GUA} \) Guaiacol
- \( \text{CAT} \) Catechol
- \( \text{CH}_4 \) Methane
- \( \text{MeOH} \) Methanol
- \( \text{CYC} \) Cyclopentanone
- \( \text{H}_2\text{O} \) Water
- \( \text{PHE} \) Phenol
- \( A_1 \) pre-exponential factor
- \( C_D \) drag coefficient
- \( u_{mf} \) minimum fluidisation velocity, \( m/s \)

**Greek symbols**

- \( \alpha_q \) volume fraction
- \( \rho_q \) density, \( \text{kg/m}^3 \)
$\nu_q$ velocity, m/s

$\tau_q$ viscous stress tensor, Pa

$\sigma$ acceleration due to gravity, m/s²

$K_{fs}$ fluid–solid momentum exchange coefficient

$P$ pressure, Pa

$\Theta_q$ granular temperature, m²/s²

$I$ stress tensor

$k_{\Theta_s}$ diffusion coefficient for granular energy, kg/sm

$\gamma_{\Theta_s}$ collision dissipation of energy, kg/s³m

$d_s$ diameter of solid particles, m

$e_{ss}$ coefficient of restitution

$g_{\rho,ss}$ radial distribution

$\lambda_s$ solids bulk viscosity, kg/ms

$\mu_q$ shear viscosity, kg/ms

**Declarations**

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**Conflicts of interest/Competing interests (include appropriate disclosures):**

- Herewith authors declare that there is no conflict of interests of their work reported in this manuscript

**Availability of data and material (data transparency):**

- Data and equations related to this work have been included in the supplementary information of the manuscript

**Code availability:**
This work has been carried out using ANSYS Fluent software and the plotting of figures have been done using MS Office Excel software. The manuscript has been prepared using MS Office Word software.

Authors' contributions:

- Mr. Ogene Fortunate has done the simulations using the ANSYS Fluent and prepared a first draft.
- Prof. Nanda Kishore has designed the problem, received funding for the project, supervised the project, edited and corrected the manuscript and checked similarity index using Turnitin.com which reported only 12% similarity.

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Table 1
Summary of physical properties of phase mixture species and their mass fractions at initial condition used during simulations of guaiacol HDO.

| Phase mixture   | Compound          | Molecular weight kg/K-mol | Entropy of formation J/kgmol-K | Density kg/m$^3$ | Heat Capacity J/kg-K | Thermoconductivity W/(m-K) | Viscosity kg/m-s | Mass fraction (no units) |
|-----------------|-------------------|---------------------------|--------------------------------|------------------|----------------------|---------------------------|-----------------|-------------------------|
| Oil phase mixture | Guaiacol (**)     | 124.139                   | 194336                         | 1128.7           | 2701.938             | 0.0215                    | 6.68e-06        | 1                       |
|                 | Cyclopentanone (**) | 84.118                   | 313560                         | 944.3            | 1780562              | 0.148454                  | 0.001073838     | 0                       |
|                 | Phenol            | 9.41E+01                  | 314730                         | 1                | *                    | 0.0454                    | 1.72E-05        | 0                       |
|                 | Catechol (**)     | 110.112                   | 333460                         | 1344             | 3194.757             | 0.168                     | 5.54e-06        | 0                       |
|                 | Methanol          | *                         | *                              | *                | *                    | *                         | *               | *                       |
| Gas phase mixture | Carbon monoxide   | 2.80E+01                  | 197531.6                       | 1.1233           | 1039                 | 0.025                     | 1.75E-05        | 0                       |
|                 | Methane           | *                         | *                              | *                | *                    | *                         | *               | *                       |
|                 | Water             | *                         | *                              | *                | *                    | *                         | *               | *                       |
|                 | Hydrogen gas      | 2.016                     | 188.7                          | 0.08988          | 14300                | 0.182                     | 1.37E-05        | 1                       |
| Solid phase mixture | Glass beads      | 61.96                     | 194336                         | 2500             | 800                  | 0.8                       | 1.70E-05        | 0.998                   |
|                 | Palladium catalyst | 160.42                    | 37820                          | 12023            | 161.95               | 71.8                      | 1.70E-05        | 0.002                   |

* (Source: Fluent 14.5), ** (Ref. 44 & 45.)
Table 2
Typical flow conditions of bio-oil and H₂-gas at different WHSV for each operating temperature and pressure used during the present simulations.

| WHSV (h⁻¹) | H₂-gas mass flow inlet (kg/s) | H₂-gas velocity inlet (m/s) | Bio-oil mass flow inlet (kg/s) | Bio-oil velocity inlet (m/s) |
|------------|-------------------------------|----------------------------|--------------------------------|----------------------------|
| 1          | 3.78E-04                      | 7.50E-02                   | 2.00E-05                       | 2.40E-07                   |
| 1          | 7.57E-04                      | 1.50E-01                   | 2.00E-05                       | 2.40E-07                   |
| 1          | 1.26E-03                      | 2.50E-01                   | 2.00E-05                       | 2.40E-07                   |
| 3          | 3.78E-04                      | 7.50E-02                   | 5.00E-05                       | 7.20E-07                   |
| 3          | 7.57E-04                      | 1.50E-01                   | 5.00E-05                       | 7.20E-07                   |
| 3          | 1.26E-03                      | 2.50E-01                   | 5.00E-05                       | 7.20E-07                   |
| 5          | 3.78E-04                      | 7.50E-02                   | 8.00E-05                       | 1.20E-06                   |
| 5          | 7.57E-04                      | 1.50E-01                   | 8.00E-05                       | 1.20E-06                   |
| 5          | 1.26E-03                      | 2.50E-01                   | 8.00E-05                       | 1.20E-06                   |

Table 3
Activation energy (Eₐ,i) and pre-exponential factors (Aᵢ) for HDO of guaiacol at different operating temperatures [34].

| Reaction, i | Temperature | 548 K | 573 K | 598 K |
|-------------|-------------|-------|-------|-------|
| GUA → CAT + CH₄ | 1.26E+08    | 1.29E+15 | 1.93E+15 | 1.26E+15 |
| CAT → PHE + H₂O | 9.98E+07    | 1.01E+11 | 1.32E+11 | 1.01E+11 |
| GUA → PHE+MeOH | 9.27E+07    | 2.13E+12 | 2.43E+12 | 2.14E+12 |
| GUA → CYC+CO+CH₄ | 1.49E+08    | 1.76E+17 | 2.68E+17 | 1.73E+17 |
| CAT → CYC+CO   | 1.25E+08    | 4.45E+05 | 3.82E+05 | 4.48E+05 |
**Fig. 1.** Schematic illustration of a fluidized bed reactor used in this study.

**Fig. 2.** Combined effects of grid, drag models and comparison of the present bed expansion ratio with the literature [33] counterparts under identical conditions.
Fig.3. Combined effects of grid size, time step and drag models on time average height of fluidized bed at superficial velocity $u = 0.38 \text{ m/s}$. 
Fig. 4. Mass fraction of HDO products of guaiacol as a function of WHSV at different temperatures and constant H$_2$-gas velocity (u=0.075 m/s).
Fig. 5. Mass fraction of HDO products of guaiacol as a function of WHSV at different temperatures and constant H$_2$-gas velocity (u=0.25 m/s).
Fig. 6. Mass fraction of HDO products of guaiacol at T=548 K as a function of H₂-gas velocity at different WHSV.
Fig. 7. Mass fraction of HDO products of guaiacol at T=598 K as a function of H\(_2\)-gas velocity at different WHSV.

Fig. 8. Distribution of reactant and products of guaiacol HDO at u=0.075 m/s and T=573 K.