Electronic Supplementary Information

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

By

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Conservation equations

The combined effect of fluid flow, heat transfer and chemical reactions occurring during HDO of 2-HB in the fluidized bed reactor make hydrodynamics problem very complex. This phenomenon is accounted by solving equations of conservation of mass (continuity equation), momentum, energy due to heat transfer and transport of chemical species implementing the multiphase Eulerian approach. The multiphase Eulerian assumes penetrating continua between the phases such that the sum of volume fractions of both phases (liquid bio-oil, solid catalyst and H_2-gas) is unity. The governing equations are summarised in Table S1. The interphase momentum exchange coefficients are provided in Table S2 while the interphase energy equations are supplied in Table S3. The other constitutive equations derived from kinetic theory of granular flow (KTGF) are used to close the governing equations; and are provided in Table S4.

Table S1

Governing equations

Parameter	**Equation**
Continuity equation of each phase q	$\frac{\partial}{\partial t}\left(\alpha_q \rho_q\right) + \nabla \cdot \left(\alpha_q \rho_q \overrightarrow{v_q}\right) = 0$
Conservation of fluid-fluid momentum of fluid phase *q* from n-fluid phases	$\frac{\partial}{\partial t}\left(\alpha_q \rho_q \overrightarrow{v_q}\right) + \nabla \cdot \left(\alpha_q \rho_q \overrightarrow{v_q}\,\overrightarrow{v_q}\right) =$ $-\alpha_q \nabla P + \nabla \cdot \overline{\overline{\tau}}_q + \alpha_q \rho_q \vec{g} + \sum_{p=1}^{n}\left(K_{pq}(\vec{v}_p - \vec{v}_q)\right)$
Conservation of fluid-solid momentum of the sth solid phase	$\frac{\partial}{\partial t}\left(\alpha_s \rho_s \overrightarrow{v_s}\right) + \nabla \cdot \left(\alpha_s \rho_s \overrightarrow{v_s}\,\overrightarrow{v_s}\right) =$ $-\alpha_s \nabla P - \nabla P_s + \nabla \cdot \overline{\overline{\tau}}_s + \alpha_s \rho_s \vec{g} + \sum_{l=1}^{n}\left(K_{ls}(\vec{v}_l - \vec{v}_s)\right)$
Conservation of energy	$\frac{\partial}{\partial t}\left(\alpha_q \rho_q h_q\right) + \nabla \cdot \left(\alpha_q \rho_q \vec{v}_q h_q\right) =$ $\alpha_q \frac{\partial p_q}{\partial t} + \overline{\overline{\tau}}_q : \nabla \vec{v}_q - \nabla \cdot \vec{q}_q + s_q + \sum_{p=1}^{n}\left(\frac{6k_q \alpha_p (1-\alpha_p)}{d_p{}^2}\left(T_p - T_q\right)\right)$

Conservation of species	$\frac{\partial}{\partial t}\left(\rho^q \alpha^q Y_i^q\right) = -\nabla \cdot \alpha^q \vec{J}_i^{\,q} + \alpha^q R_i^q + \alpha^q S_i^q$

In turbulent flows for instance due to transition of flow regimes because of fluidisation like in this present study, mass diffusion calculated as:

$$\vec{J}_i = -\left(\rho D_{i,m} + \frac{\mu_t}{Sc_t}\right)\nabla Y_i - D_{T,\mathrm{i}} \frac{\nabla T}{T}$$

where Sc_t is the turbulent Schmidt number defined as $Sc_t = \frac{\mu_t}{\rho D_t}$ where μ_t is the turbulent viscosity , D_t is the turbulent mass diffusivity, $D_{i,m}$ is the mass diffusion coefficient for species "i" in the mixture and D_T is the thermal diffusion coefficient at temperature *T*.

The correlations for fluid-fluid momentum exchange coefficients from Schiller-Neumann [28] drag correlations are provided in Table S2(a). Similarly, Table S2(b) summarises the fluid-solid momentum- exchange coefficient as presented by Gidaspow model [20] (recommended for dense fluidised beds). This model is a combination of Wen and Yu [21] and Ergun [22] drag model equations for solid phase.

Table S2

Correlations of interphase momentum exchange coefficients

(a) Fluid-fluid	**(b) Fluid-solid**
$K_{pq} = \frac{\alpha_p \alpha_q \rho_p f}{\tau_p}$ where	$k_{ls} = 150 \frac{\alpha_s \left(1-\alpha_l\right)\mu_l}{\alpha_l d_s^2} + 1.75 \frac{\rho_l \alpha_s \left\lvert \vec{v}_s - \vec{v}_l \right\rvert}{d_s}$
$\tau_p = \frac{\rho_p d_p^2}{18\mu_q}$ and $f = \frac{C_D \mathrm{Re}}{24}$	for $\alpha_l < 0.8$ (Ergun equation)
$C_D = \begin{cases} \frac{24}{\mathrm{Re}}\left(1 + 0.15\,\mathrm{Re}^{0.687}\right); & \mathrm{Re} \le 1000 \\ 0.44; & \mathrm{Re} > 1000 \end{cases}$	For $\alpha_l > 0.8$, it is calculated from Wen-Yu model as; $K_{ls} = \frac{3}{4} C_D \frac{\alpha_s \alpha_l \left\lvert \vec{v}_s - \vec{v}_l \right\rvert}{d_s} \alpha_l - 2.65$

where $\mathrm{Re} = \dfrac{\rho_q \left| \vec{v}_p - \vec{v}_q \right| d_p}{\mu_q}$ where $C_D = \dfrac{24}{\alpha_l \, \mathrm{Re}_s} \left[1 + 0.15 \left(\alpha_l \, \mathrm{Re} \right)^{0.687} \right]$

Table S3 gives the Ranz-Marshall [23] and Gunn [24] model equations (where p = s in case for granular flow) to calculate the Nusselt number for fluid-fluid (bio-oil-hydrogen gas) and fluid-solid (hydrogen gas- catalyst) interphase energy transfer respectively.

Table S3

Interphase energy equations for fluid-fluid [23] and for fluid-solid interaction [24]

$$\mathrm{Nu}_p = 2.0 + 0.66 \mathrm{Re}_p^{1/2} \mathrm{Pr}^{1/3}$$

$$Nu_s = \left(7 - 10\alpha_f + 5\alpha_f^2\right)\left(1 + 0.7 \mathrm{Re}_s^{0.2} \mathrm{Pr}^{1/3}\right) + \left(1.33 - 2.4\alpha_f + 1.2\alpha_f^2\right) \mathrm{Re}_s^{0.7} \mathrm{Pr}^{1/3}$$

$$\mathrm{Pr} = \frac{c_p \mu_q}{k_q}$$

The Prandtl number in the Gunn [24] model is defined as in Ranz-Marshall[23]model with $q = f$.

Table S4

Constitutive equations derived from KTGF

Phase stress-strain tensor

$$\bar{\bar{\tau}}_q = \alpha_q \mu_q \left(\nabla \vec{v}_q + \nabla \vec{v}_q^{\,T} \right) + \alpha_q \left(\lambda_q - \frac{2}{3} \mu_q \right) \nabla \cdot \vec{v}_q \bar{\bar{I}}$$

Fluctuation energy conservation of solid particles

$$\frac{3}{2} \frac{\partial}{\partial t} (\rho_s \alpha_s \Theta_s) + \nabla \cdot (\rho_s \alpha_s \vec{v}_s \Theta_s) = (-p_s \bar{\bar{I}} + \bar{\bar{\tau}}_s) : \nabla \cdot \vec{v}_s + \nabla \cdot (\mathrm{k}_{\Theta_s} \nabla \Theta_s) - \gamma_{\Theta_s} + \phi_{ls}$$

Diffusion coefficient of granular energy

$$\mathrm{k}_{\Theta_s} = \frac{150 \rho_s d_s \sqrt{\Theta_s \pi}}{384 (1 + \mathrm{e}_{ss}) \mathrm{g}_{o,ss}} \left[1 + \frac{6}{5} \alpha_s g_{o,ss} \left(1 + e_{ss} \right) \right]^2 + 2 \rho_s d_s \alpha_s^2 g_{o,ss} \left(1 + \mathrm{e}_{ss} \right) \sqrt{\frac{\Theta_s}{\pi}}$$

Collision dissipation energy

$$\gamma_{\Theta_s} = \frac{12 \left(1 - e_{ss}^2 \right) g_{o,ss}}{d_s \sqrt{\pi}} \rho_s \alpha_s^2 \Theta_s^{3/2}$$

Table S4 *continued*

Radial distribution function
$g_{o,ss} = \left[1 - \left(\frac{\alpha_s}{\alpha_{s,\max}}\right)^{1/3}\right]^{-1}$
Transfer of kinetic energy
$\phi_{ls} = -3K_{ls}\Theta_s$
Solids pressure
$p_s = \alpha_s \rho_s d_s \Theta_s + 2\rho_s (1+e_{ss})\alpha_s^{2} g_{o,ss}\Theta_s$
Solids bulk viscosity
$\lambda_s = \frac{4}{3}\alpha_s \rho_s d_s g_{o,ss}(1+e_{ss})\sqrt{\frac{\Theta_s}{\pi}}$
Solids shear
$\mu_s = \mu_{s,col} + \mu_{s,kin} + \mu_{s,fr}$
Collisional viscosity
$\mu_{s,col} = \frac{4}{5}\alpha_s \rho_s d_s g_{0,ss}(1+e_{ss})\left(\frac{\Theta_s}{\pi}\right)^{1/2}\alpha_s$
Kinetic viscosity
$\mu_{s,\mathrm{kin}} = \frac{\alpha_s d_s \rho_s \sqrt{\Theta_s \pi}}{6(3-e_{ss})}\left[1 + \frac{2}{5}(1+e_{ss})(3e_{ss}-1)\alpha_s g_{0,ss}\right]$
Frictional viscosity
$\mu_{s,\mathrm{fr}} = \frac{p_s \sin\phi}{2\sqrt{I_{2D}}}$