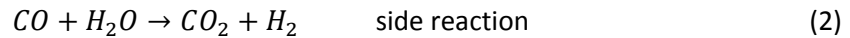
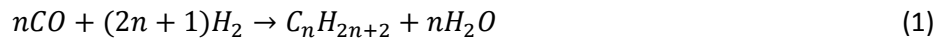


Problem Statement

Background

Most chemical processes require catalysts to provide more feasible routes for faster and more selective chemical reactions to take place. In heterogeneous catalysis, heat and mass transfer may limit surface reaction kinetics. One chemical process that received much attention in the last decade from researchers and industries around the world is Fischer-Tropsch synthesis (FTS), which is a process in which liquid hydrocarbons (such as gasoline and diesel fuel) are formed by polymerizing lighter hydrocarbons produced from syngas (a mixture of carbon monoxide, CO, and hydrogen, H₂). This technology is represented by the following chemical reaction,



One challenge with this reaction is to make the catalyst as much selective as possible, meaning that the production of the liquid hydrocarbons (desirable products) should be favored over the production of carbon dioxide and methane (the undesirable products). Iron-based catalysts are cheap materials that proved to be good choices of selective and active catalysts. However, improvements on these catalysts should be studied to further enhance their activity and selectivity.

Previous studies performed by our research group on the water-gas shift (WGS) activity of iron-based catalysts have shown that the rate of carbon dioxide production is given by the following Langmuir-Hinshelwood model,

$$r_{CO_2} = \frac{kK_{CO}K_{H_2O}([CO][H_2O] - [CO_2][H_2]/K)}{(1 + K_{CO}[CO] + K_{H_2O}[H_2O] + K_{CO_2}[CO_2] + K_{H_2}[H_2])^2} \quad (3)$$

$$k = Arr \cdot \exp\left(-\frac{E_a}{R_g \cdot T}\right) \quad (4)$$

$$K(T \text{ } ^\circ\text{C}) = 0.0196 T^2 - 11.661 T + 1778.9 \quad (5)$$

where r_{CO_2} is the reaction rate for production of carbon dioxide, k is the rate constant, K_i is the adsorption equilibrium constants for species i , K is the WGS reaction equilibrium constant, $[i]$ is the concentration or partial pressure of species i in the reactor system, Arr is the Arrhenius constant, E_a is the activation energy, R_g is the universal gas constant, and T is the reaction temperature. Table 1 shows the values of each constant with varying percentages of carbon dioxide.

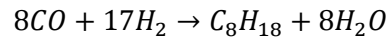
Table 1
Parameters for the Langmuir-Hinshelwood model

Wt% of La ₂ O ₃	E_a (kJ/mol)	Arr (mol/min)	K_{CO} (L/mol)	K_{H_2O} (L/mol)	K_{CO_2} (L/mol)	K_{H_2} (L/mol)
0%	103	457000	604	1278	4064	4064
0.5%	86	27980	937	1094	3699	3699

5%	69	560	367	717	1494	1494
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Optimization problem

The chemical reaction is:



Design variables and objective function

In this problem, we would like to maximize the effectiveness factor of the reaction rate (η) for the production of octane (C_8H_{18}), at 15% CO conversion, by varying the agglomerate particle size diameter (d_p), reaction temperature (T), reaction pressure (P), the volumetric flow rate of the feed gas (\dot{V}_{in}), and H_2/CO feed ratio (R) at the three different compositions or (wt %) of lanthanum oxide (x). These variables would change the internal and external heat transfer rates, and the pore diffusion calculations. We would not worry about external mass transfer limitations and would assume to be negligible. With regards to pore diffusion resistance, η can be maximized by minimizing the Weisz-Wheeler modulus (M_w).

Design variables: $d_p, T, P, R, \dot{V}_{in}, x$

1- $d_p > 100 \mu m$

This constrains the particle diameter to be greater than $100 \mu m$ to prevent extreme pressure drops and to prevent plugging reactor in case really small mesh sizes are not available to hold the catalyst.

2- $T \leq 300 \text{ }^\circ C$

This constrains the operating or reaction temperature to be less than the temperature at which the catalyst starts to deactivate. It should fall in the range of what has been recommended in the literature for active iron-based FTS catalysts.

3- $P \leq 405 \text{ psi}$

The upper constrain has been put to make sure that water and octane are still in the gas phase at the highest reaction pressure possible.

4- $y_{CO} \leq 0.6$

This constrains the composition of CO to be less than 0.6, to make sure that the sum of all mole fractions is less than 1, considering 0.4 wt% is diluting Helium.

5- $\dot{V}_{in} \leq 150 \text{ cm}^3 / \text{min}$

This would limit the entering flow rate of reacting gases so that the CO conversion remains under 0.15 for the differential reactor assumption to be valid.

6- $x = 0, 0.5, \text{ and } 5 \text{ wt}\%$

Different loadings of lanthana depending on the water-gas shift activity results of iron-based catalysts.

Objective function: M_w

Design functions

Objective function

$$\text{Minimize } M_w = L_p^2 \cdot \frac{n+1}{2} \cdot \frac{r_{CO} \cdot \rho_p / [CO]}{V_{pore} \cdot D / \tau}$$

Pore diffusion limitations – Internal Mass transfer

The wheeler's modulus (M_w) for cylindrical particles is given by,

$$L_p = d_p / 4$$

$$R = y_{H_2} / y_{CO}$$

$$y_{H_2} = 1 - y_{CO} - y_{He}$$

$$r_{CO} = \frac{X_{CO} \cdot \dot{V}_{in} \cdot y_{CO} \cdot P_o}{R_g \cdot T_o \cdot W_{cat}} - r_{CO_2} / 100 W_{cat}$$

$$[CO] = \frac{y_{CO} \cdot \dot{n}_{in} \cdot (1 - X_{CO})}{\dot{V}_{in} \cdot (1 + \delta \cdot y_{CO} \cdot X_{CO})}$$

$$[H_2] = \frac{y_{H_2} \cdot \dot{n}_{in} - (v_{H_2} / -v_{CO}) y_{CO} \cdot \dot{n}_{in} \cdot X_{CO}}{\dot{V}_{in} \cdot (1 + \delta \cdot y_{CO} \cdot X_{CO})}$$

$$[H_2O] = \frac{(v_{H_2O} / -v_{CO}) \cdot y_{CO} \cdot \dot{n}_{in} \cdot X_{CO}}{\dot{V}_{in} \cdot (1 + \delta \cdot y_{CO} \cdot X_{CO})}$$

$$[CO_2] = [H_2O]$$

$$\delta = \Sigma v_i / -v_{CO}$$

$$\dot{n}_{in} = \dot{V}_{in} \cdot P_o / (R_g \cdot T_o)$$

$$\frac{1}{D} = \frac{1}{D_{AB}} + \frac{1}{D_K}$$

$$D_{AB}(\text{cm}^2/\text{s}) = 0.001853 \frac{T^{1.5} \left(\frac{1}{M_{CO}} + \frac{1}{M_{H_2}} \right)^{0.5}}{P \cdot \sigma_{comb}^2 \cdot \Omega_{comb}}$$

$$\sigma_{comb} = \frac{\sigma_{CO}/\text{\AA} + \sigma_{H_2}/\text{\AA}}{2}$$

$$\Omega_{comb} = \frac{1.06036}{T^{*0.15610}} + \frac{0.193}{\exp(0.47635 T^*)} + \frac{1.03587}{\exp(1.52996 T^*)} + \frac{1.76474}{\exp(3.89411 T^*)}$$

$$T^* = T/\epsilon_K$$

$$\epsilon_K = \sqrt{\epsilon_{KH_2} \cdot \epsilon_{KCO}}$$

$$D_K \left(\frac{\text{cm}^2}{\text{s}} \right) = 4850 \cdot \frac{d_{pore}}{\text{cm}} \cdot \sqrt{\frac{T/\text{K}}{M_{CO}/\text{g} \cdot \text{mol}^{-1}}}$$

$$M_{mix} = M_{CO} \cdot y_{CO} + M_{H_2} \cdot y_{H_2} + M_{He} \cdot y_{He}$$

where r_{CO} is the rate of CO consumption, L_p is the characteristic length, D_{AB} is the bulk diffusivity, D_K is the Knudsen diffusivity, V_{pore} is the pore volume, d_{pore} is the pore diameter, n is the reaction order, \dot{n}_{in} is the inlet molar flow rate of the feed stream, X_{CO} is the conversion of CO, \dot{V}_{in} is the inlet stream volumetric flow rate, ν_i is the stoichiometric reaction constant for the corresponding species, σ_i is the intermolecular distances for the corresponding species, Ω_{comb} is the collision integral between CO and H_2 , y_i is the mole fraction of the corresponding species in the feed stream, M_{mix} is the molecular of the feed mixture, and τ is the tortuosity.

Internal heat transfer limitations

$$\beta = \frac{(\epsilon_p \cdot (-\Delta H_r) \cdot D/\tau) \cdot [CO_s]}{T_s \cdot k_e}$$

$$CO_s = [CO] \left(\frac{T_{reac}}{T_s} \right)$$

$$T_s = T + \Delta T_{film}$$

$$\Delta T_{film} = (-\Delta H_r) \cdot r_{CO} \cdot L_p/h$$

$$h = j_H \cdot C_{p_stream} \cdot \rho_g \cdot v_g \cdot (Pr)^{-2/3}$$

$$j_H = 2.19 Re^{-2/3} + 0.78 Re^{-0.381}$$

$$Pr = C_{pstream} \cdot \mu_g / (k_e \cdot MW_{mix})$$

$$Re = \rho_g \cdot MW_{mix} \cdot v_g / (a \cdot \mu_g \cdot \psi)$$

$$v_g = \dot{V}_{in} / (A_{react})$$

$$\varepsilon_p = \rho_p \cdot V_{pore}$$

$$\rho_p = \rho_b / (1 - \varepsilon_b)$$

$$\varepsilon_b = \rho_b \cdot V_{pore}$$

$$A_{react} = \pi d_{react}^2 / 4$$

$$a = 4(1 - \varepsilon_b) / d_p$$

$$\rho_g = (\rho_T + \rho_P)$$

$$\rho_T \left(\frac{mol}{m^3} \right) = 0.580375 \cdot \left[0.0013 \left(\frac{T}{^\circ C} \right)^2 - \left(1.2967 \frac{T}{^\circ C} \right) + 590.15 \right]$$

$$\rho_P \left(\frac{mol}{m^3} \right) = 0.393453 \cdot \left(0.9409 \frac{P}{psi} + 1.8171 \right)$$

$$\mu_g \left(\frac{g}{cm \cdot s} \right) = -10^{-9} \left(\frac{T}{^\circ C} \right)^2 + 10^{-6} \frac{T}{^\circ C} + 0.0001$$

where β is the particle temperature difference, ΔH_r is the heat of reaction, T_s is the surface temperature of the catalyst, k_e is the effective thermal conductivity coefficient of the catalyst, h is the convective heat transfer coefficient, j_H is the Chilton-Colburn factor for packed-bed flow, Re is the Reynold's number of the flowing gases, v_g is the stream's velocity, SA_{cat} is the catalyst's surface area, ρ_g is the stream's density, ρ_T is the temperature dependence term for density, ρ_P is the pressure dependence term for density, μ_g is the stream's viscosity.

External Mass transfer limitations

$$MT_{ext} = r_{CO} \cdot \rho_p \cdot L_p / (k_c \cdot [CO])$$

$$k_c = j_D \cdot v_g \cdot (Sc)^{-2/3}$$

$$Sc = \frac{\mu_g}{\rho_g \cdot D_{AB} \cdot MW_{mix}}$$

where, MT_{ext} is the external mass transfer coefficient, and k_c is the mass transfer coefficient.

Constraints

The constraints on this problem would be to sustain negligible internal and external heat and mass transfer rates under reaction conditions. These would translate into:

$$\beta \leq 1 \text{ } ^\circ\text{C}$$

$$\Delta T_{film} \leq 1 \text{ } ^\circ\text{C}$$

$$MT_{ext} \leq 0.1$$

$$R > 0.67$$

Parameters

$$\epsilon_{KH_2} = 38 \text{ K}$$

$$\epsilon_{KCO} = 110 \text{ K}$$

$$\sigma_{CO} = 3.59 \cdot 10^{-10} \text{ m}$$

$$\sigma_{H_2} = 2.915 \cdot 10^{-10} \text{ m}$$

$$M_{CO} = 28.01 \text{ g/mol}$$

$$M_{H_2} = 2 \text{ g/mol}$$

$$M_{H_e} = 4.002 \text{ g/mol}$$

$$\tau = 3$$

$$\rho_b = 0.9 \text{ g/mL}$$

$$T_o = 298.15 \text{ K}$$

$$P_o = 102941 \text{ Pa, the ambient pressure in Provo}$$

$$R_g = 8.31447 \text{ L}\cdot\text{kPa}/(\text{mol}\cdot\text{K}) = 8.31447 \text{ J}/(\text{mol}\cdot\text{K})$$

$$d_{pore}, V_{pore}, SA_{cat} =$$

Table 2 pore volumes and sizes of the three different catalysts

Wt% of La ₂ O ₃	SA _{cat} (m ² /g)	d _{pore} (Angstroms)	V _{pore} (cm ³ /g)
0	157.9	35.5	0.140
0.5	135.7	44.1	0.149
5	143.6	39.2	0.141

$$\nu_{CO} = -8$$

$$\nu_{H_2} = -17$$

$$\nu_{O_2} = 1$$

$$\nu_{H_2O} = 8$$

$$y_{He} = 0.4$$

$k_e = 8 \text{ W/m}^2\text{K}$, the effective thermal conductivity of cementite (Fe_3C).

$$X_{CO} = 0.15$$

$$W_{cat} = 0.05 \text{ g}$$

$$C_{p_stream} = 26.331 \text{ J/(mol}\cdot\text{K)}$$

$$d_{reac} = 3/8 \text{ in}$$

$$\psi = 0.92$$

$$\Delta H_r = -1306 \text{ kJ/mol}$$

Notes:

The stream's density changes insignificantly with the stream's composition.

The heat of reaction changes insignificantly with the reaction temperature, reaction pressure, and inlet's stream composition.

The heat capacity of the gaseous stream changes insignificantly with temperature, pressure and composition.

All empirical formulae were derived from more general and complex calculations performed in Mathcad and are only true for the temperature range of 200 °C – 300 °C.