

## **Development of Hydrodynamic and Heat Transfer Profiles for Fischer–Tropsch Synthesis in a Fixed Bed Reactor of Different Scales**

**Dr. Mohammed A. Atiya Al Saraj**

Ministry of Higher Education and Scientific Research/Baghdad

Email: mohatiya1965@yahoo.com

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### **ABSTRACT**

Comprehensive hydrodynamic and heat transfer study of Fischer–Tropsch synthesis (FTS) on a home-based cobalt catalyst, with the presence of water–gas shift (WGS), is conducted with a fixed bed reactor. Two different diameters have been used for the reactor, 4 and 7 inches. To meet the requirements of industrial applications, simulation has been used to scale up the effect on the commercial scale reactor. Synthetic gas was used as a feed stream and its conversion to H<sub>2</sub> was considered. Temperature and velocity profiles were obtained for the different scales.

**Keywords:** Fisher Tropsch, hydrodynamics, heat transfer, scaling up, cobalt catalyst

### **INTRODUCTION**

**F**ischer–Tropsch synthesis (FTS) process is recognized as very appealing methods for product the petrochemicals and ultra-clean liquid fuels. In contrast, it is proper for addressing environmentally friendly pollution problem and remote gas application [1]. (FTS) is the process, which can be, used to product the hydrocarbons from H<sub>2</sub>/CO feed mixture and usually considered as a promising method for the product of the clean fuels. It observed that the most common catalysts for the FT reaction are Fe and Co [2]. Nevertheless, there is important attention to locate different catalysts for fuels yield with SO<sub>x</sub> and NO<sub>x</sub> emission reductions [3]. Recently transition metal carbides and molybdenum carbide have attracted important consideration as preferred options for various catalytic reactions, i.e. NH<sub>3</sub> synthesis [4], hydro-treating [5], NO reduction [6], and methane reforming [7] since the discovery by Levy and Boudart [8]. The process conditions of the Fischer-Tropsch Synthesis are widely performed, especially in research studies. Typical conditions are pressures between 10-60 bar and temperatures in the range of 200-350 °C [9-11].

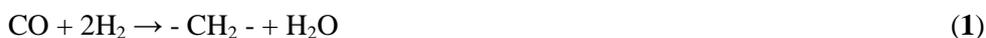
Many catalyst types have been used to obtain liquid fuel productivity, such as cobalt (Co), iron (Fe), nickel (Ni) and ruthenium (Ru). A few criteria must be met to achieve the optimal catalyst performance: the activity, selectivity and other characteristics [12]. In addition to the variation in catalyst types, such as iron (Fe), cobalt (Co), nickel (Ni) and ruthenium (Ru), to achieve the optimum product selectivity, only the first three catalysts appear to be economically feasible for large-scale applications [13]. Each source of feedstocks used to yield syngas in FTS has its own merits and demerits, which occasionally dictate the syngas production, processing and catalyst selection. Perhaps, when the feedstock is biomass, ultimate analysis of the biomass may dictate the use of either gasification or pyrolysis. In addition, it very important to use of iron over cobalt with low hydrogen production potential of biomass against natural gas because the previous water-gas-shift reactor (WGSR), increases the partial pressure of H<sub>2</sub>, thus changing the H<sub>2</sub>:CO ratio for better catalytic performance.

Just, the FTS is at the center of efforts to produce drop-in fuels from biomass, mainly JP-8/jet fuels for the aviation industry [14]. It can be concluded that BTL catalytic conversion via the process of FTS will not need any changes in the current infrastructure of the automotive [14].

Mostly, the cobalt based catalysts kinetics current different expressions when it was compared with the iron-based catalysts. Furthermore, the kinetic equations are established on the rate-determining step, which includes a dual-site surface reaction. Ruthenium (Ru) -based catalysts were prepared by the sol–gel technique for biomass-to liquid (BTL) operation and had their performance tested under different conditions [15].

Narataruksa et al. [16] initiated a work to develop a new chemical reactor design in which well distribution of gaseous reactants and hydrocarbon yields could be achieved, and led to higher output and conversion. The catalytic study was carried out in two steps using a simple and reliable method. In the first step, the effects of reaction temperatures and inlet H<sub>2</sub>/CO molar feed ratios obtained from biomass gasification were investigated on the catalyst performance. A set of experimental results obtained in a laboratory fixed bed reactor was described and summarized. Moreover, a simplified Langmuir–Hinshelwood–Hougen–Watson (LHHW) kinetic model was proposed with two promising models, where the surface decomposition of carbon monoxide was assumed as the rate-determining step (RDS) [17].

The Fischer-Tropsch synthesis can be described by the following, simple reaction [18-19].



Equation 1 represents FTS reaction and equation 2 is for water-gas reaction, which can be neglected when the cobalt catalyst is used.

FTS reactors required various methods to accomplish the control of the temperature and acquire a better choice of the catalyst and reaction products.

Large numbers of variables would affect the hydrodynamic and transport parameters of FT reaction and hence the performance of fixed bed reactor such as design variables (e.g., dimensions, geometry, catalyst activity and strength, heat duty, and quality of the product) and operating variables (e.g., gas velocity, liquid flow rate if significant, liquid loops and recycle rates, catalyst loading, feed conditions and composition, catalyst renewal rate, pressure, temperature, etc.). The key hydrodynamic and transport parameters in fixed bed reactor that affect directly the reactor performance are overall gas holdup ( $\epsilon_g$ ), gas holdup radial profile ( $\epsilon_{g,r}$ ), and fluid velocity ( $u_f$ ), and heat transfer coefficient ( $h$ ). There is a big change between these parameters for laboratory, pilot and commercial scales. For the first two, they can be obtained by experimental readings and the third one can be estimated using the available and reliable correlations and based on the findings risks/benefits and possible consequences will be deduced. It is noticeable that most of hydrodynamic and heat transfer studies had been conducted on mimic columns using air as a fluid and beads as a catalyst loading. Therefore, the obtained effects were not reliable and not well understood. The behavior is complex in the presence of catalyst instead the plastic beads and the working on real components of chemical reaction will demonstrate the effects of operating and design variables in the presence of reaction sites on transport parameters.

In the present study, comprehensive study will be conducted on fixed bed reactor of Fisher Tropsch system using Iraqi synthesis gas (H<sub>2</sub>/CO) on a homemade Co catalyst. This study targets the effect of different reactor scales on hydrodynamic and heat transfer parameters using sophisticated measurement techniques and apparatuses.

## Experimental Work

### Feedstock (Synthesis gas)

Synthesis gas (SG) used in this study was obtained from the First Global Company of Fertilizers in Iraq at 20 bar pressure and the cylinder was pressurized up with nitrogen to 75 bar. The physical properties of the SG are explained in Table 1.

**Table (1) Composition of synthetic gas (SNG)**

Physical property	SNG
Hydrogen, H <sub>2</sub> %	43.96
Carbon dioxide, CO <sub>2</sub> %	22.87
Carbon monoxide, CO%	45.82
Methane, CH <sub>4</sub> %	1.04
Hydrogen sulfide, H <sub>2</sub> S ppmv	23.48
Carbonyl sulfide, COS, ppmv	195.36
Heat of composition, Btu/sef (HHV)	284.8

**Nitrogen**

99.999% purity nitrogen gas was supplied by National Oxygen Pte Ltd and used without further purification.

**Hydrogen**

99.999% purity nitrogen gas was supplied by National Oxygen Pte Ltd and used without further purification.

**Catalyst**

The chemical compounds used to prepare the catalyst in this study, as follows:

**Active compound utilized in the catalyst preparation**

For catalyst preparation, the specifications of the used chemicals and materials are shown in Table 2.

**Table (2). Specifications of the chemicals and materials used in the study**

Materials and chemicals	Purity%	Purpose	Production
Cobalt nitrate Co(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O	99.5	Active material	Alpha chemical
Deionized water	-	Solvent of the materials	Summaraa company

**Alumina oxide ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>)**

Table 3, presented the alumina oxide (type gamma alumina ( $\gamma$ )) specifications which is used as a carrier in the production of the catalyst.

**Table (3) Specifications of ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>)**

Characteristics	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>
Pore volume, (cm <sup>3</sup> /g)	0.5367
Bulk density, (g/cm <sup>3</sup> )	0.671
Surface area, (m <sup>2</sup> /g)	289
Diameter, (mm)	1.6
Shape	Sphere

**Catalyst used in the experiment**

The solution of cobalt supported on alumina (Al<sub>2</sub>O<sub>3</sub>) was prepared by incipient wetness impregnation (IWI). Firstly and prior to IWI, 200 gm of cobalt chloride was dried in the oven (Thermo Fisher Scientific, Max, heating 500 °C, US) at 130°C for 2 hours to remove the moisture from alumina. Secondly, 5.6 gm from cobalt chloride is added to 150 cm<sup>3</sup> deionized

water, and stirred with at room temperature for one hour. The pretreated gamma alumina in step one is put in the flask under evacuation condition (using vacuum pump) in order to remove gases out of support pores, then the cobalt chloride solution is added to gamma alumina at the rate of (15-20) drop per minute with continuous stirring until all the solution is saturated. With a water bath, the temperature is kept constant at (100°C). Then the saturated gamma alumina has been dried overnight in the oven at (130°C). Calcination requested for five hours in the oven at (550°C) under air laminar flow. The metal salts loaded on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were converted into the equivalent metal oxides, which lead to deposit of active metal oxide over catalyst support along with acquiring desired physiochemical properties of the catalyst. Calcination step is completed in *Fertilizer/Northern Company- Baiji*.

### H<sub>2</sub> analysis (thermal conductivity)

H<sub>2</sub> percentage in SG before and after a run is evaluated in accordance with thermal conductivity. The estimation of unreacted H<sub>2</sub> outlet concentration could be accomplished by reading the value in feed gas and exit streams with portable gas analyzer (model K6050, HITECH Company, UK). The measuring of the gas percentage is founded on its thermal conductivity of H<sub>2</sub>, which defiantly varies from the other components.

The non-depleting cathetometer sensor, which might be fixed inside the gas trap, measures the thermal conductivity. The sensor incorporates an exceedingly sensitive part of low thermal capacity. Signal processing is given a microprocessor (accuracy  $\pm 1\%$  of span, stability up to 1% fsd/month). After 20 tests, calibration is required to guarantee the system's inherent and high stability. The provided ranges related to the gas being measured but could be from high ppm to 100%. In this experimental study, the operating conditions are set as for the optimum performance, the sample flow rate was ranges from 100 to 300ml/min, while the sample temperature range from  $-10$  to  $+55^\circ\text{C}$  (non-condensing), and the sample pressure is 3 barg maximum.

### Experimental setup

The catalytic reaction was conducted in tubular fixed bed reactor (I.D= 4 inches and 7 inches, L= 75 cm and 100 cm) 316 L adapted stainless steel which is externally heated with a ceramic beaded electrical resistance coil put into grooves on the external reactor to provide temperature through the reactor. The reactor and the heating coil were covered with a layer of insulation to prevent heat loss. The temperature of the reactor was controlled by temperature controller type PID model DT105 by Gemo Company. The temperature setting for different types of catalysts was achieved using a J-type thermocouple in the center of the bed. The flanges were welded on both ends and metal supports were welded 23 mm from the bottom of the tube. The temperature was measured by placing the tip of the thermocouple attached to the outside wall of the stainless steel tubing. The outlet downstream from the reactor are fed to a cooling system (temperature set up to  $-10^\circ\text{C}$ ) temperature was controlled by temperature controller model LT102 by Gemo Company to control the temperature of separator to separate liquid from gases. The outlet gases are passed through variable flow meter by Brooks Instruments N.V. Veenendaal, and then the effluent gases pass through an online gas analyzer to measure the hydrogen percentage in the exit stream (unreacted gas). The pressure transducer probe has been used to measure pressure difference and obtain the gas holdup. The wire heat transfer probe has been used to measure heat transfer coefficient. The ceramic balls were put under the catalyst (CoMo/Al<sub>2</sub>O<sub>3</sub>) then ceramic bed above the catalyst bed. Figure 1 shows a schematic diagram the experimental setup.

### Experimental runs

A- 10.000 g cat (dry base) of the catalyst sample was weighed.

B- The catalyst was placed inside the reactor on a small ball of ceramic on the screen at the bottom of the bed then bed of small pieces of ceramic beads.

C- Up stream of nitrogen with 5 L/h was fed to the reactor to heat the system to the experimental temperature using the heating system.

D- The temperature controller was turned on and set to the desired temperature using calibration curve. The temperature increased in range 10 °C / min until it reached to 400 °C

E- The hydrogen percentage in the outlet gas stream samples has been recorded with portable gas analyzer.

F-Flow of 5 L/h of 25% hydrogen and 75% of nitrogen was introduced to the reactor at 1 bar pressure. Catalyst reduction was continued for 4 hrs.

G- Then, hydrogen stream was switched off and the reactor has been cooled down to 170 °C.

H-The synthesis gas ( $H_2/CO = 4$ ) was fed into the reactor. However, slow temperature ramping was used during startup to avoid reactor runaway. The nitrogen was turned off.

I-The syngas was turned off after the time of run is closed to 30 min and small stream of nitrogen flowed through the system until the reactor temperature was below 30 °C. Figures 1-a and 1-b show schematic diagram and picture of experimental setup.

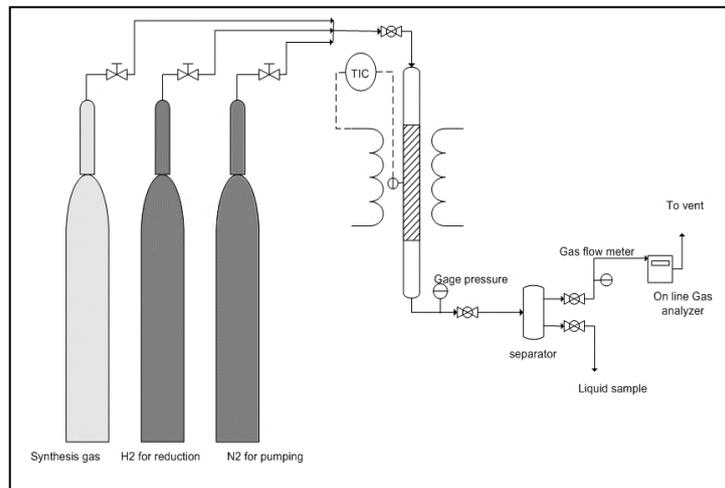


Figure (1-a) Schematic diagram of experimental setup

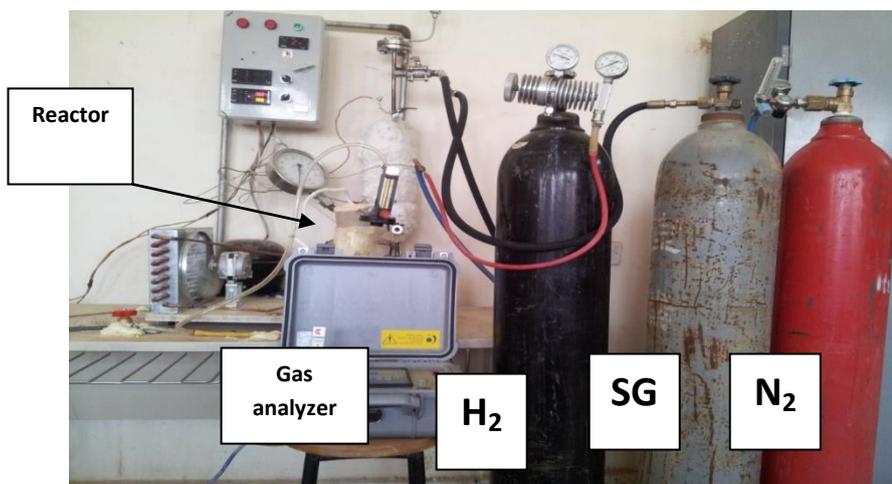


Figure (1-b). Picture of experimental setup

**Results and Discussion**

**Effect of radial distance on hydrodynamics**

Overall gas holdup increases slightly with radial direction and it has been observed in Figure 2 for the given reaction conditions for two different laboratory column diameters (R is the maximum diameter for each column, 4 or 7 inches, and r is the local diameter) at 20 cm/s gas velocity. This increase can be attributed to the increase in solids loading would result in enhancing of the bubble coalescence due to increase in the apparent viscosity of the fluid as a result of fuel formed hence the transition from the bubbly flow regime to churn turbulent flow regime occurs at a lower gas velocity [19]. At a lower SG velocity, overall gas holdup reduces with solids with radial direction the radial gas holdup profile magnitude becomes lower, but little sharper at lower gas velocity and its sharpness does not much change or would be a little flattered at the higher range of gas velocity.

For the estimation of the effect on a commercial scale, Satterfield [20] developed a correlation for fixed bed reactor based on pressure drop:

$$\frac{\Delta P}{h} \left( \frac{g_c \rho d_p^3}{\mu^2} \right) \left( \frac{\epsilon}{1-\epsilon} \right)^3 = \frac{Re}{1-\epsilon} \left[ \alpha + \beta \frac{Re}{1-\epsilon} \right] \tag{3}$$

It is observed from Figure 2 that the estimated overall gas holdup in the commercial unit is lower than that of the laboratory scale reactors despite the gas velocity are higher in the industry. This is would be due to the effect of high catalyst loading and the low either L/D or the uncertainty of the correlation prediction. The radial gas holdup profile in the commercial unit is sharper than the two in experimental apparatus with higher local gas holdup at the center region of the column. Since the dynamics of the gas dictate the hydrodynamics of the fixed bed reactor and drives the chemical reaction (production of denser fluid, the fuel), it is expected an enhanced gas circulation in the commercial unit. This may attribute to the buoyancy effect between the central region and the wall region of the column due to the sharper slope of radial gas holdup profile. This has been also shown from the radial profile of the liquid/slurry velocity in both experimental and commercial units where the slop of the radial profile of the slurry velocity is sharper in the commercial unit compared to the experimental units. This will enhance interaction between the phases, SG and catalyst, and a benefit for commercial unit in terms of mass and improving heat transfer. Nevertheless, it enhances adversary effects on the reactor and catalyst performance due to low L/D that may encounter. However, in FT synthesis the shortcoming of low gas-liquid mass transfer coefficient and can be offset if the reactant gases (CO and H<sub>2</sub>) saturate the liquid. Furthermore, the presence of internals benefits mass transfer by reducing the bubbles coalesce and hence increasing the specific interfacial area and the bubble frequency. The rate of renewal surface between the gas and liquid enhances in the commercial unit.

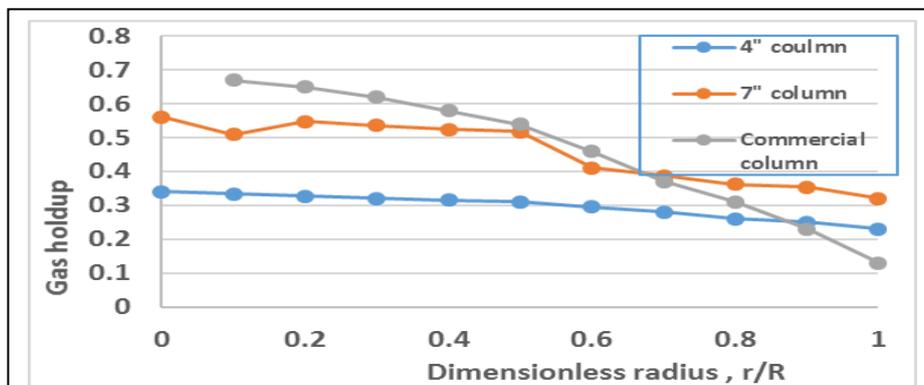


Figure (2) Effect of scale of on radial gas hold up of different scales of FT reactors at 20 cm/s gas velocity

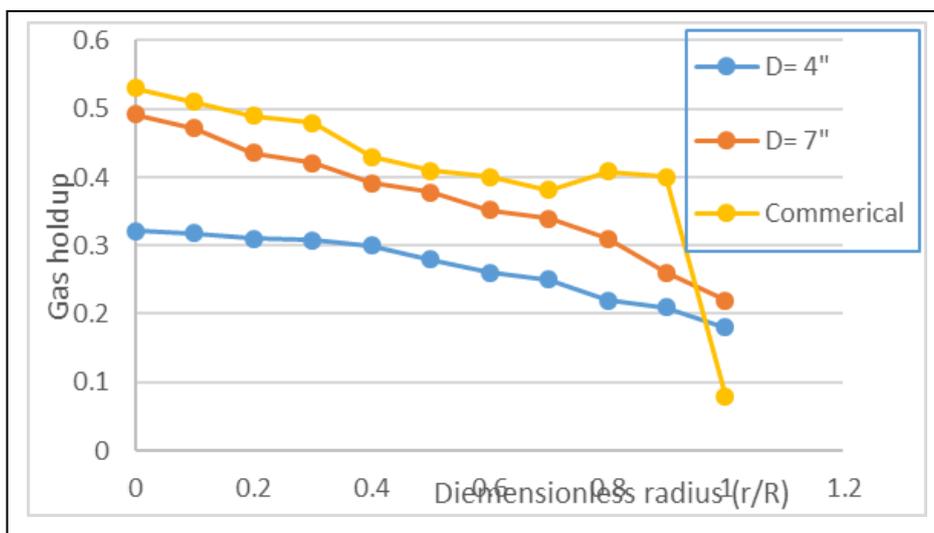


Figure (3) Effect of scale of on radial gas hold up of different scales of FT reactors at 18 cm/s gas velocity

For lower gas flow rate,  $u = 18$  cm/sec, the radial gas hold is shown in Figure 3 and increases with radial direction due to less occupation of gas phase against the solid phase. Even with higher scale, the behavior is similar and  $L/D$  ratio with the commercial column affects the behavior too.

**Effect of radial distance on heat transfer coefficient**

The profile of heat transfer coefficient along the radial direction of different scales of reactors is shown in Figure 4. Heat transfer coefficient has been calculated by the assumption of homogeneity is reasonable when  $Bi$  is smaller than 0.1, expressed as:

$$Bi = \frac{hL_c}{k_b} \tag{4}$$

Where:

$h$  = film coefficient or heat transfer coefficient or convective heat transfer coefficient

$L_c$  = characteristic length, which is commonly defined as the volume of the body divided by the surface area of the body,

$k_b$  = thermal conductivity of the catalyst particle.

The increase in column diameter increases the weight of catalyst that should be loaded and make the solid phase more intensive in throughout the interaction regions. Thus, for commercial scale it would be better to damp the gas circulation due to enhance and/or enhance diffusion and enlarge the free area of flow, reaction and heat evolved. However, based on different amount of feed, catalyst loaded and free area available for reaction, heat transfer coefficient for commercial scale is greater than two times the corresponding value of laboratory scale. Unfortunately, no data are available in the literature for such important effects for the purpose of comparison. However, presence of considerable amounts of catalyst will increase the area of reaction (reactive sites) and would enhance the interaction among phases for the benefit of the transport parameters (heat and mass transfer) in the commercial unit. In addition, the presence of more catalyst reduces the bubble coalescence and improved the specific interfacial area (gas-solid surface area per unit volume) for mass and heat to transfer [21]. In addition, the bubble frequency would be enhanced causing an improvement on the heat to transfer from the reaction mixture to the heat exchanging tubes surface that is equipped along the reactor for cooling.

These would improve the heat transfer and hence in better operation of the commercial unit at the isothermal condition compared to laboratory scale reactors.

Moreover, the rate of renewal surface between the gas and solid enhances in the commercial unit. The estimated heat transfer coefficients in the commercial unit are higher than those in laboratory units. Based on radial profile of gas on solid heat transfer coefficient in Figure 5 for a gas velocity of 18 cm/sec, the radial profile of the heat transfer coefficients has been estimated which is higher in magnitude than that of the experimental units and has the same trend of higher heat transfer coefficient in the center of the column and lower in the wall region. This is expected since the presence of catalyst as mentioned above reduces bubble coalescence, narrowing the bubble size distribution and increasing the bubble frequency, which enhances the renewal surface between reaction mixture and the surface of heat exchanging tubes.

**Axial heat transfer profile in laboratory and Commercial unit**

For the purpose of comparison and assessing the effect of scaling up, the correlation has been developed to predict the axial heat transfer coefficient for different column scales. This correlation is based on film density,  $\delta$ , mass transfer coefficient,  $k$ , thermal diffusivity,  $\alpha$ , and temperature of operation [22]:

$$h = \frac{2k}{\sqrt{\pi\alpha t_c}} + \left[ e^{\frac{\alpha t_c}{\delta^2}} \left( 1 - \operatorname{erf} \frac{\sqrt{(\alpha t_c)}}{\delta} \right) - 1 \right] \tag{5}$$

The axial profile of heat transfer coefficient for different scales of reactors is shown in Figure 6 at 20 cm/sec. The effect of going from the inlet, beginning of chemical reaction, toward the outlet, end of the packed column, is obvious in Figure 6. As conversion increases, the rate of a chemical reaction increases too, and more heat of chemical reaction is liberated. As successive chemical reaction proceeds, the heat evolved increases temperature of the reaction mixture and rate constant increases consequently based on Arrhenius equation.

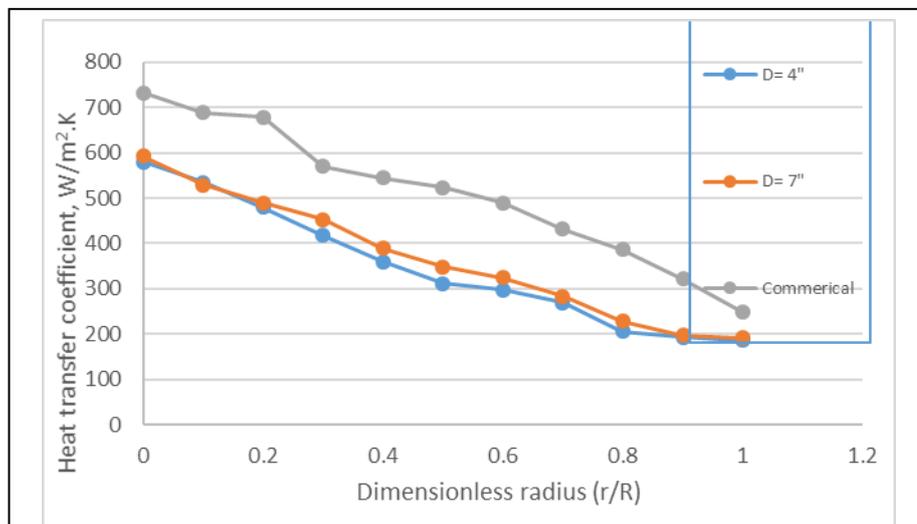


Figure 6 Axial heat transfer profile in laboratory and Commercial unit scales of FT reactors at 20 cm/s gas velocity

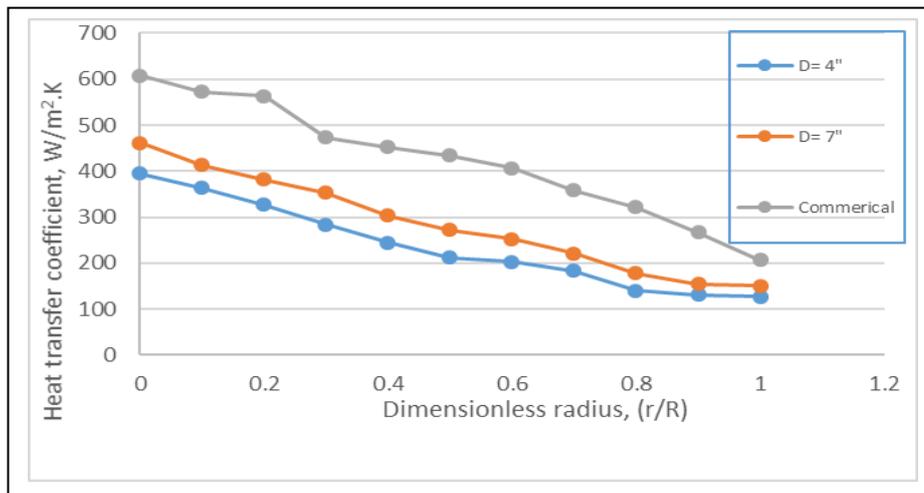


Figure (5) Effect of radial distance on heat transfer coefficient of different scales of FT reactors at 18 cm/s gas velocity

The trend of increase for the commercial unit is similar to the laboratory units. If velocity has been reduced to a lower value, heat transfer coefficient gets decreases due to simultaneous effect between momentum and heat transfer [23]. Figure 7 shows this effect of lowering velocity on the heat transfer coefficient for different scales of columns compared to Figure 6.

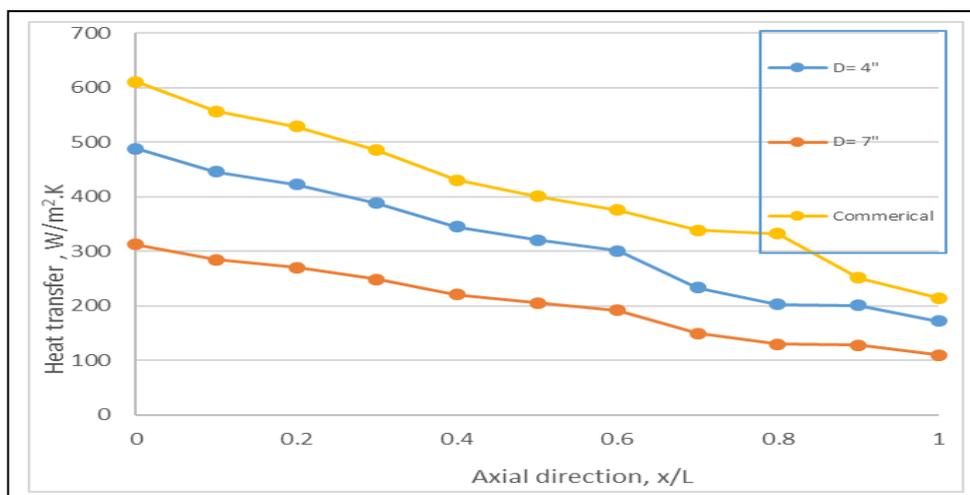
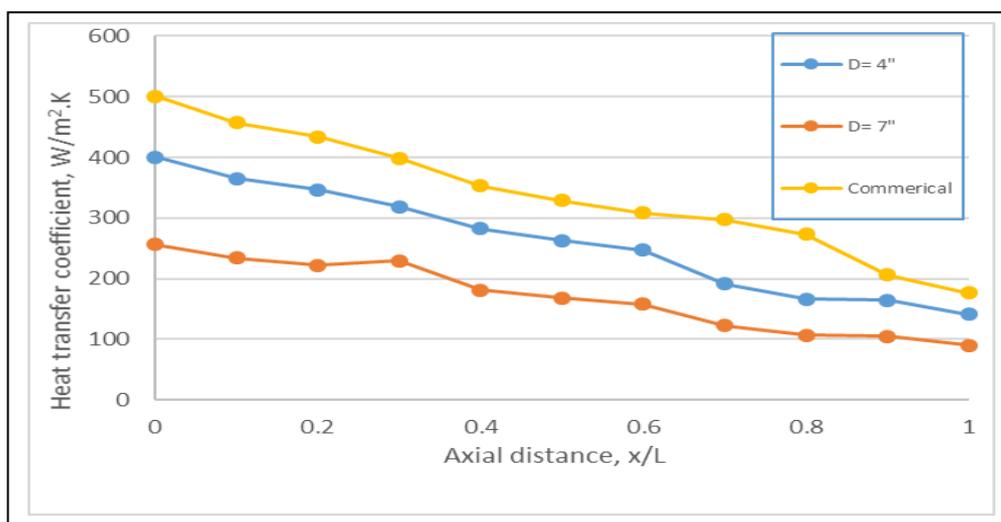


Figure (6) Effect of axial distance on heat transfer coefficient of different scales of FT reactors at 20 cm/s gas velocity



**Figure (7) Effect of axial distance on heat transfer coefficient of different scales of FT reactors at 18 cm/s gas velocity**

## CONCLUSIONS

Commercial unit will be operated at higher gas velocity and higher catalyst weight compared to the laboratory unit and hence the flow regime will be deep in churn turbulent flow regime compared to laboratory units, which is within the early conditions of the churn turbulent flow regime. The flow regime is characterized with intense interaction between phase and back mixing. Gas holdup increases slightly with diameter and it has been reported and shown that after a column of 7 inches in diameter there would be no much changes in gas holdup with diameter if the conditions remain the same. However, it has been shown by numerous researchers [2, 3, 20-23] that loading more catalyst will enhance the bubble coalescence. Gas holdup reduces with increasing catalyst. Since the dynamics of the gas dictate the hydrodynamics of the fixed bed reactor drives gas flow, it is expected an enhanced gas recirculation in the commercial unit due to the buoyancy effect between the central region and the wall region of the column due to the sharper slope of radial gas holdup profile. From the slope of the radial profile of the gas holdup, which is higher in the commercial unit as per the correlations predictions compared to those of the laboratory units, the commercial unit would operate in deeper churn turbulent flow regime compared to the laboratory unit, which help enhance back mixing and interaction among phases. However, enhanced back mixing is not desired in FT synthesis [24] and could be considered as part of the risks outlined below. The increased back mixing inside the commercial unit compared with the laboratory units, which would affect negatively on the CO conversion and CO<sub>2</sub> selectivity as it will be outlined in the risks and mitigation. It is noteworthy to mention that the correlations were developed based on empty column. The results of the present study show that radial gas holdup profile would be close to each other in the column with different column diameters (4 and 7 inches) if the gas velocity and the volumetric gas flow rate are matched based on the free cross sectional area to flow. In this case the small column need less volumetric flow rate to match the gas velocity in the large column. Due to enhanced interactions among phases and improved bubble frequency, narrower bubble size distribution, and improved renewal surface rate, heat transfer from the liquid/solid to the surface of the heat exchanging tubes would be enhanced in the commercial. This causes better control of the temperature and the isothermal conditions. Hence, the reactor

performance in terms of conversion, productivity (possible selectivity) and the catalyst age and conditions would be benefited in a commercial unit.

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