Accepted Manuscript

Intensifying The Fischer-Tropsch Synthesis By Reactor Structuring - A Model Study

N. Hooshyar, D. Vervloet, F. Kapteijn, P.J. Hamersma, R.F. Mudde, J.R. van Ommen

Please cite this article as: N. Hooshyar, D. Vervloet, F. Kapteijn, P.J. Hamersma, R.F. Mudde, J.R. van Ommen, Intensifying The Fischer-Tropsch Synthesis By Reactor Structuring - A Model Study, *Chemical Engineering Journal* (2012), doi: http://dx.doi.org/10.1016/j.cej.2012.07.105

Intensifying The Fischer-Tropsch Synthesis By Reactor Structuring - A Model Study

N. Hooshyar[1], D. Vervloet, F. Kapteijn, P.J. Hamersma, R.F. Mudde and J.R. van Ommen

Department of Chemical Engineering, Delft University of Technology, Julianalaan 136, 2628 BL, the Netherlands.

Abstract

This paper investigates the intensification of Fischer-Tropsch Synthesis in two types of three-phase catalytic reactors: slurry bubble columns and multi-tubular fixed beds. A simple mathematical model is used to analyse the effect of structuring on the C_{5+} productivity of these two types of reactors. The results of the model show that decreasing the backmixing with a factor 4 and increasing the gas residence time in a slurry bubble column considerably enhances the production of C_{5+}. On the other hand in a fixed bed reactor a similar improvement is obtained when the heat transfer coefficient is improved with a factor 2.5 and the diffusion length in catalyst particles is decreased with a factor 2. Both reactors show a potential improvement in productivity per reactor volume; 20% in the slurry bubble column and 40% in the fixed bed reactor.

Keywords: slurry bubble column; fixed bed; Fischer- Tropsch; process intensification; structured reactors

1. Introduction

Intensifying the operation of slurry bubble columns and multi-tubular fixed beds can be achieved by structuring. The advantage of a structured reactor is that it may be designed in full detail up to the local surroundings of the catalyst, allowing ultimate precision [1]. Such a rational design can strongly enhance the productivity of three-phase reactors.

Typical challenges in a slurry reactor are reducing backmixing and optimising solids separation, while in a multi-tubular fixed bed reactor these are improving temperature gradients and catalyst effectiveness. Several methods have been proposed to structure the systems with a fixed catalyst

---

[1]e-mail of the corresponding author:n.hooshyar@tudelft.nl

9 structure [1–8] and systems with a mobile catalyst [9–13]. In each of these approaches, structur-

10 ing introduces extra degrees of freedom to optimize the design objectives independently [14].

11 In this paper we show how reducing the backmixing in a *Slurry Bubble Column* (SBC) and im-

12 proving the heat transfer and lowering the diffusion length in a *Fixed Bed* (FB) improves the

13 productivity of a reactor. Moreover, we illustrate, using a simple model, what gains can be ex-

14 pected when these bottlenecks are relieved by structuring. We use the Fischer-Tropsch Synthesis

15 (FTS) as a working example for this purpose. The results demonstrate that the potential for in-

16 creasing the productivity per reactor volume for both reactor types is tens of %.

17

18 2. Structuring

19 Structuring as a way of process intensification has been proposed for different type of industrial

20 reactors in which three phases of gas-liquid-solid are present [15, 16]. Although the structuring

21 is more common in the area of fixed catalyst reactors [4, 5] , it can be also applied in fluidized

22 beds [17] and slurry bubble columns [9, 18].

23 The backmixing of both gas phase and slurry phase in a SBC is detrimental to conversion and

24 selectivity. By restricting the vortical structures, for examples by injecting the gas bubbles with a

25 narrow size distribution and with approximately the same velocities [9, 19], we constrict the res-

26 idence time distribution, increase the average residence time and therefore, intensify the process.

27 Fig. 1 shows a photo of a needle sparger that has been used in a SBC for process intensification.

28 In another example of structuring a SBC, Maretto and Krishna [20] modelled and optimized a

29 staged reactor for FTS. Their results show that using sieve plates, they can approach plug flow

30 condition instead of well-mixed.

31 We study the effect of the liquid backmixing on the output of the SBC. We use a typical axial

32 dispersion coefficient of the liquid phase, $E_{L,SB}$, for a non-structured system for the base case.

33 It is obtained using the relation proposed by Deckwer et al. [21]:

$$E_{L,SB} = 0.768 U_{sg}^{0.32} D_{T,SB}^{1.34} \tag{1}$$

34 As can be seen in the Eq. (1) the liquid axial dispersion coefficient is dependent on the super-

35 ficial gas velocity, U_{sg}, and reactor diameter, $D_{T,SB}$. In our base case with U_{sg}=0.3 m/s and

2

36 $D_{T,SB}$=7.5 m, we find that $E_{L,SB}$=7.77 m^2/s.

37 Cheng et al. [22] investigated the reduction of backmixing in a bubble column by interrupting

38 the global liquid circulation and eliminating the downward flow of the liquid. They have reported

39 that installation of four channels at different heights of the column (i.e., local restriction of the

40 column diameter) causes a strong reduction in the liquid backmixing.

41 Cheng et al.[22] measured the residence time distribution (RTD) of the liquid to test the effect

42 of channels on the liquid backmixing in a bubble column. They used the tanks-in-series model

43 to interpret their results and introduced the tank number N and the dimensionless variance for

44 the liquid flow σ_θ^2. Their results show that by structuring, the number of stirred tanks in series

45 increases from 1.4 to 3.2 and the dimensionless variance decreases from 0.7 to 0.3. Because of

46 the linear relation between the dimensionless variance and axial dispersion coefficient [23], the

47 $E_{L,SB}$ would decrease about 60% .

48 Dreher and Krishna [12] studied the influence of partition plates on the liquid backmixing in bub-

49 ble columns with different diameters and different gas velocities. They staged the columns with

50 perforated brass plates and determined the RTD of the liquid phase. They reported that using

51 partition in a bubble column and staging it, the magnitude of the liquid circulation and therefore

52 the $E_{L,SB}$ can be decreased by 90%. The reason would be restricting the liquid circulation be-

53 tween the compartments.

54 In the case of multi-tubular FB reactors, diffusion length and heat transfer are the most important

55 challenges. Long diffusion lengths (catalyst effectiveness <1) give an ineffective use of the re-

56 actor volume. Large temperature gradients lead to non-uniform behaviour in terms of selectivity,

57 activity and deactivation. These points can be alleviated by replacing a bed of random particles

58 by structured catalyst packings [1]. An example of structured packing in a FB was studied by

59 Vervloet et al. [5]. Their investigation on cross flow structured packing elements shows that

60 these types of packings can greatly improve the radial heat transport characteristics compared to

61 randomly packed beds. In practice this leads to much flatter temperature profiles. Furthermore,

62 using a structured catalyst support allows decoupling of the diffusion length from pressure drop

63 effects, similar to monolith packings, effectively negating costly pressure losses, while realizing

64 a degree of freedom in catalyst design. Fig. 2 represents two types of such packings.

65

66   [Figure 1 about here.]

3

67 [Figure 2 about here.]

68 **3. Model**

69 To facilitate a fair comparison between the two reactor types we used the same simple 1-D

70 model for both SBC and FB. For this purpose, i.e. a qualitative exploration and comparison

71 of the production sensitivity of certain reactor specific characteristics, the use of a 1D model

72 is sufficient [24]. Although more detailed modelling approaches are available - such as a 2D

73 modelling approach for the FB [24], which is more precise in predicting, for example, reactor

74 runaway behavior the added value for our objective would be negligible. For the SBC, we

75 distinguish the slurry phase consisting of liquid and mono dispersed particles, the large bubble

76 phase and the small bubble phase [20, 25]. We assume the absence of mass transfer limitations

77 inside the small SBC catalyst particles ($d_p = 50\mu m$) and a catalyst effectiveness of 1[21]. For the

78 FB, we assume that the gas and liquid are in equilibrium, while the most important mass transfer

79 limitations are inside the relatively large catalyst particles ($d_p = 2mm$)[6]. We take internal

80 transport limitations into account by calculating the catalyst effectiveness factor (typically <1)

81 from a reaction-diffusion perspective [26], which can vary with the reactor coordinate.

82 In the case of the multi-tubular FB reactor it is sufficient to model one single tube, since it is

83 reasonable to assume the same behaviour for each tube. Fig. 3 shows a schematic representation

84 of the model for both SBC and FB.

85

86 [Figure 3 about here.]

87 The mathematical model for mass and heat transfer in the SBC and FB is presented in Table 1

88 and operating conditions [6, 27, 28] have been summarized in Table 2.

89

90 [Table 1 about here.]

91 We describe the FTS using the rate expression of Yates and Satterfield [29]:

92

$$R_{CO} = F\nu_{CO}\frac{aP_{CO}P_{H_2}}{(1 + bP_{CO})^2} \tag{2}$$

4

93 in which:

94

$$a = a_0 exp[4494.41(\frac{1}{493.15} - \frac{1}{T})] \qquad (3)$$

$$b = b_0 exp[-8236(\frac{1}{493.15} - \frac{1}{T})] \qquad (4)$$

95 where a_0=8.8533x10$^{-3}mol/s.kg_{cat}bar^2$, b_0=2.226 $1/bar$, ν_{CO}=-1 and ν_{H_2}=-2. We introduce

96 a multiplication factor F=3 to account for improvements in FTS-catalyst activity [30] since the

97 publication of this rate expression.

98

99 [Table 2 about here.]

4. Results and Discussions

101 By solving the coupled sets of design equations the performance of both reactors are determined

102 at steady state conditions. In both reactor types the probability factor of hydrocarbon chain

103 growth , α, is considered to be constant (α=0.9) which is a simplification for the FB [26]. The

104 α determines the C_{5+} selectivity, which can be calculated through: $S_{C5+} = 1 - \sum_{n=1}^{4} n(1 -$

105 $\alpha)^2\alpha^{n-1}$.Since α is assumed constant value, we can calculate the S_{C5+} value immediately,

106 which is 0.92. In the following sections, we will calculate the conversion for the different cases.

107 Combined with the C_{5+} selectivity, this gives us the productivity for the different cases.

108

4.1. Slurry bubble column reactors

110 Guided by the previous studies [12, 22], we characterize to what extent the reducing axial dis-

111 persion by structuring affects the syngas conversion. The different cases we have considered for

112 the sensitivity analysis in a SBC have been summarized in Table 3-a. We chose a base case (case

113 1, unstructured, backmixing properties following Eq. 1) superficial gas velocity of 0.3 m/s and

114 compared the C_{5+} productivity to a reactor that was operated with reduced backmixing proper-

115 ties as a consequence of structuring (case 2, structured reactor, 75% reduced backmixing). The

116 same production sensitivity analysis was performed for an increased superficial gas velocity of

117 0.4 m/s - case 3 (unstructured, backmixing effects according to Eq. 1) and case 4 (structured

5

118 reactor, 75% reduced backmixing). The results show that in a SBC a 75% decrease in the liquid

119 axial dispersion coefficient both from case 1 to case 2 and from case 3 to case 4 yields a higher

120 final syngas conversion (see Fig. 4). The backmixing causes the differences in the syngas con-

121 centration in different heights of the reactor and consequently the lower conversion in the lower

122 part of the reactor than in the higher part. Increasing the superficial gas velocity (case 1 to case

123 3 and case 2 to case 4) lowers the conversion, but increases the productivity (see Table 4).

124

125 [Figure 4 about here.]

126 [Table 3 about here.]

4.2. Fixed bed reactors

128 Previous studies on structuring the FB reactors done by Pangarkar et al. [1, 3, 4] and Vervloet

129 et al. [5] on cross-flow structured packings show that using such structures improve the overall

130 heat transfer (U_{ov}) performance of the FB from 400 (W/m^2K) (randomly packed bed, cases 1

131 and 3) to 1000 (W/m^2K) (structured packing, cases 2 and 4). This catalyst support structure

132 allows for a shorter catalyst diffusion length (d_p), which we will also exploit in our modelling

133 analysis. We decrease the particle diameter, d_p in case 2 and 4 from typically 2.0 mm to 1.0 mm

134 to study the influence of the diffusion length. Table 3-b contains the four cases studied for the FB

135 reactor. For the temperature control in the FB two criteria have been imposed: (1) we consider

136 a maximum allowed temperature of 510 K, both for the selectivity and safety (runaway) issues,

137 and (2) the average bed temperature is as close to 498 K as possible satisfying the first restriction

138 - by varying the inlet temperature ($T_{in} = T_c$).

139 Fig. 5 shows the conversion profiles in the fixed bed reactor for cases 1 - 4. The results indicate

140 that a decrease in the particle diameter from 2.0 mm to 1.0 mm (case 3) or an improvement in

141 the heat transfer (case 2) only marginally increase the syngas conversion compared to the base

142 case. However, when both parameters are varied (case 4) a significant improvement is found. To

143 explain this, we investigate the axial temperature profiles of the FB (Fig. 6).

144 Cases 1 and 2 are temperature limited as they reach the 510 K constraint, due to limited heat

145 removal. Because of significant heating of the fluids with the axial reactor coordinate a rela-

146 tively low inlet and cooling temperature have to be chosen. This leads to a lower than desired

147 average reactor temperature, and therefore limits the overall productivity. Cases 3 and 4 show

6

148 much flatter axial temperature profiles, due to the improved heat transfer coefficient, that are not

149 bound by the upper temperature limit. The relatively flat temperature profiles allow for a higher

150 inlet and cooling temperature to reach the desired average bed temperature, without violating the

151 maximum temperature constraint.

152

153 [Figure 5 about here.]

154 [Figure 6 about here.]

155 *4.3. Opportunities for process intensification for both reactor types*

156 In this section, we will compare the two reactor types side by side. It should be noted that we did

157 not further optimize the reactor performance by varying the flow rates, the syngas composition,

158 or separate optimization of the cooling and inlet temperature, which may alter the reactor perfor-

159 mance to a certain extent.

160

161 [Figure 7 about here.]

162 Fig. 7 gives the normalized *STY* relative to the base case. Reducing the liquid dispersion and

163 increasing the gas velocity increases the *STY* of C_{5+} for a SBC, while decreasing the diffusion

164 length and increasing the heat transfer increases the *STY* for the FB. The results show that the

165 FB reactor has a potential of increasing the STY of C_{5+} with over 40% and SBC over 20%. We

166 emphasize that the conversion in the regular (non-structured) SBC is already higher than the FB

167 (88% versus 53% for the base cases), making the room for improvement is smaller in case of a

168 SBC. In industry, FBs for Fischer-Tropsch synthesis are typically operated in series.

169 Table 4 gives the space time yield (*STY*) of C_{5+} (the targeted product fraction) for all the four

170 cases in both SBC and FB reactors. The table shows that hydrocarbon production per unit of

171 catalyst mass is roughly equal for both reactor types. However, reactor volume without and with

172 considering the cooling volume, STY' and STY'', in all four cases is considerably higher for

173 the FB than for the SBC. The productivity of C_{5+} per reactor volume considering the cooling

174 volume, is for a FB is about two times that of for a SBC.

175

7

176 [Table 4 about here.]

177 Instead of increasing the conversion for a given reactor configuration, one can also consider to
178 reduce the reactor volume at keeping the conversion constant. For the FB comparing case 4 with
179 the base case in Fig. 5 shows that we can reduce the reactor volume with 40% while keeping
180 the same conversion as in the base case. The improved heat transfer (flatter temperature profile)
181 can also be used to increase the tube diameter, and thus reducing the number of tubes. This will
182 mean a reduction of the capital investment in case of the multi-tubular FB reactor. For the SBC
183 we consider case 2 and the base case. For plug flow with axial dispersion, the conversion at a
184 fixed axial position varies when the reactor length is changed; this makes it necessary to perform
185 an additional simulation. We calculated which reactor height is needed to reach 88% conversion
186 (base case) while the $E_L = 1.95 m^2/s$ (case 2). The results of the simulation show that the
187 reactor height can be reduced by 14%.

188

189 **5. Conclusions**

190 Using a simple 1-D model, we studied the intensification of Fischer-Tropsch synthesis in two
191 different catalytic reactors: a slurry bubble column and a fixed bed. We compared four different
192 cases for each of these reactors and varied main parameters which can improve the performance
193 of the reactors.

194 • Our model shows that by structuring both three-phase catalytic reactors can be intensified.

195 • In a slurry bubble column reactor with a conversion of 88% as the base case, a 75% de-
196 crease in the liquid axial dispersion and an increase in the gas residence time enhances the
197 productivity by 20%.

198 • In a fixed bed reactor with a conversion of 53% as the base case, the productivity can be
199 improved by more than 40% when the heat transfer coefficient is improved with a factor
200 2.5 and the diffusion length in the catalyst particles is decreased with a factor 2.

201 • In both reactor types structuring can also be used to reduce reactor volume rather than
202 increasing conversion.

203

8

Nomenclature

a_0	Kintetic parameter	$(mol/s.kg_{cat}bar^2)$
a_{large}	Gas-liquid specific area for large bubbles	(m^2/m^3)
a_{small}	Gas-liquid specific area for small bubbles	(m^2/m^3)
a_w	Cooling tube specific external surface area referred to the total reactor volume	(m^2/m^3)
b_0	Adsorption coefficient	$(1/bar)$
$C_{i,g0}$	Concentration of i in the gas phase at reactor inlet	(mol/m^3)
$C_{i,g,small}$	Concentration of i in small bubbles	(mol/m^3)
$C_{i,g,large}$	Concentration of i in large bubbles	(mol/m^3)
$C_{i,L}$	Concentration of i in liquid	(mol/m^3)
C_s	Solids volume fraction in gas free slurry	$(-)$
D_T	Column diameter	(m)
d_p	Catalyst average diameter	m
$E_{g,large}$	Axial dispersion coefficient of the large bubbles	(m^2/s)
$E_{g,small}$	Axial dispersion coefficient of the small bubbles	(m^2/s)
E_L	Axial dispersion coefficient of the liquid phase	(m^2/s)
F	Catalyst improvement factor	$(-)$
H	Reactor height	(m)
$K_{L,i,small}$	Volume mass transfer coefficient of i with small bubbles	$(1/s)$
$K_{L,i,large}$	Volume mass transfer coefficient of i with large bubbles	$(1/s)$
m_i	Henry's coefficient	$(-)$
P	Reactor pressure	(Pa)
R_i	Reaction rate expression	$(mol_i/kg_{cat}/s)$
S_{C5+}	C_{5+} selectivity by weight	$kg\,kg^{-1}$
STY	Space time yield	$(kg/kg_{cat}/h)$
STY'	Hydrocarbon production per reactor volume excluding the cooling medium	$(kg/m^3_{G+L+cat}/h)$
STY''	Hydrocarbon production per reactor volume including the cooling medium	$(kg/m^3_{reactor}/h)$
T	Temperature	(K)
T_c	Cooling temperature	(K)

9

U_{sg}	Superficial gas velocity	(m/s)
U_{ss}	Superficial slurry velocity	(m/s)
U_{ov}	Overal heat transfer	(W/m^2K)
z	Reactor coordinate	(m)
α	Probability factor of hydrocarbon chain growth	$(-)$
α_{eff}	Liquid/slurry to internal coil wall conversion heat transfer coefficient	(W/m^2K)
ε_{large}	Gas hold-up in large bubbles	$(-)$
ε_{small}	Gas hold-up in small bubbles	$(-)$
ε_{bed}	Catalyst hold-up	$(-)$
ε_L	Liquid hold-up	$(-)$
λ_{ax}	Effective axial heat conductivity of the liquid-solid suspension	(W/mK)
ν_i	Stoichiometric ratio of species i	$(-)$
ρ_p	Solid density	(kg/m^3)

References

References

[1] K. Pangarkar, T. J. Schildhauer, J. R. van Ommen, J. Nijenhuis, F. Kapteijn, J. A. Moulijn, Structured packings for multiphase catalytic reactors, Ind. Eng. Chem. Res. 47 (2008) 3720–3751.

[2] M. T. Kreutzer, F. Kapteijn, J. A. Moulijn, Fast gas-liquid-solid reactions in monoliths: A case study of nitro-aromatic hydrogenation, Catal. Today 105 (2005) 421 – 428.

[3] K. Pangarkar, T. J. Schildhauer, J. R. van Ommen, J. Nijenhuis, J. A. Moulijn, F. Kapteijn, Experimental and numerical comparison of structured packings with a randomly packed bed reactor for fischertropsch synthesis, Catal. Today 147, Supplement (2009) S2 – S9.

[4] K. Pangarkar, T. J. Schildhauer, J. R. van Ommen, J. Nijenhuis, J. A. Moulijn, F. Kapteijn, Heat transport in structured packings with co-current downflow of gas and liquid, Chem. Eng. Sci. 65 (2010) 420 – 426.

[5] D. Vervloet, M. Kamali, J. J. J. Gillissen, J. Nijenhuis, H. E. A. van den Akker, F. Kapteijn, J. R. van Ommen, Intensification of co-current gas-liquid reactors using structured catalytic packings: A multiscale approach, Catal. Today 147, Supplement (2009) S138 – S143.

[6] R. Guettel, T. Turek, Comparison of different reactor types for low temperature fischer-tropsch synthesis: A simulation study, Chem. Eng. Sci. 64 (2009) 955 – 964.

[7] C. P. Stemmet, M. Meeuwse, J. van der Schaaf, B. F. M. Kuster, J. C. Schouten, Gas-liquid mass transfer and axial dispersion in solid foam packings, Chem. Eng. Sci. 62 (2007) 5444 – 5450.

[8] P. Heidebrecht, M. Pfafferodt, K. Sundmacher, Multiscale modelling strategy for structured catalytic reactors, Chem. Eng. Sci. 66 (2011) 4389–4402.

10

[9] N. Hooshyar, P. J. Hamersma, R. F. Mudde, J. R. van Ommen, Intensified operation of slurry bubble columns using structured gas injection, Can. J. Chem. Eng. 88 (2010) 533–542.

[10] J. Ellenberger, R. Krishna, Intensification of slurry bubble columns by vibration excitement, Can. J. Chem. Eng. 81 (2003) 655–659.

[11] A. Lakota, M. Jazbec, J. Levee, Impact of structured packing on bubble column mass transfer charasteristics: Part 1. backmixing in the liquid phase, Acta Chim. Slov. 48 (2001) 453–468.

[12] A. Dreher, R. Krishna, Liquid-phase backmixing in bubble columns, structured by introduction of partition plates, Catal. Today 69 (2001) 165 – 170.

[13] D. I. Enache, G. J. Hutchings, S. H. Taylor, S. Raymahasay, J. M. Winterbottom, M. D. Mantle, A. J. Sederman, L. F. Gladden, C. Chatwin, K. T. Symonds, E. H. Stitt, Multiphase hydrogenation of resorcinol in structured and heat exchange reactor systems: Influence of the catalyst and the reactor configuration, Catal. Today 128 (2007) 26 – 35.

[14] F. Kapteijn, J. J. Heiszwolf, T. A. Nijenhuis, J. A. Moulijn, Monoliths in multiphase catalytic processes - aspects and prospects, CATTECH 3 (1999) 24–41.

[15] A. Cybulski, J. A. Moulijn, Structured catalysts and reactors, Chemical industries, Taylor & Francis, 2006.

[16] T. A. Nijhuis, M. T. Kreutzer, A. C. J. Romijn, F. Kapteijn, J. A. Moulijnk, Monolithic catalysts as more efficient three-phase reactors, Catal. Today 66 (2001) 157 – 165.

[17] J. R. van Ommen, J. Nijenhuis, C. M. van den Bleek, M.-O. Coppens, Four ways to introduce structure in fluidized bed reactors, Ind. Eng. Chem. Res. 46 (2007) 4236–4244.

[18] J. Ellenberger, J. van Baten, R. Krishna, Intensification of bubble columns by vibration excitement, Catal. Today 79-80 (2003) 181 – 188.

[19] N. Hooshyar, P. J. Hamersma, R. F. Mudde, J. R. van Ommen, Gas fraction and bubble dynamics in structured slurry bubble columns, Ind. Eng. Chem. Res. 49 (2010) 10689–10697.

[20] C. Maretto, R. Krishna, Modelling of a bubble column slurry reactor for fischertropsch synthesis, Catal. Today 52 (1999) 279 – 289.

[21] W. D. Deckwer, Y. Serpemen, M. Ralek, B. Schmidt, Modeling the fischer-tropsch synthesis in the slurry phase, Ind. Eng. Chem. Proc. D. D. 21 (1982) 231–241.

[22] Z.-M. Cheng, Y. Wu, Z.-B. Huang, Backmixing reduction of a bubble column by interruption of the global liquid circulation, Ind. Eng. Chem. Res. 48 (2009) 6558–6563.

[23] G. F. Froment, K. B. Bischoff, Chemical reactor analysis and design, Wiley, 1979.

[24] A. Jess, C. Kern, Modeling of multi-tubular reactors for fischer-tropsch synthesis, Chem. Eng. Technol. 32 (2009) 1164–1175.

[25] N. Hooshyar, S. Fatemi, M. Rahmani, Mathematical modeling of fischer-tropsch synthesis in an industrial slurry bubble column, Int. J. Chem. React. Eng. 7 (2009).

[26] D. Vervloet, F. Kapteijn, J. Nijenhuis, J. R. van Ommen, Fischer-tropsch reaction-diffusion in a cobalt catalyst particle: Aspects of activity and selectivity for a variable chain growth probability, Catal. Sci. Technol. 2 (2012) 1221–1233.

[27] J. W. A. De Swart, R. Krishna, Simulation of the transient and steady state behaviour of a bubble column slurry reactor for fischer-tropsch synthesis, Chem Eng Process 41 (2002) 35–47.

[28] S. T. Sie, R. Krishna, Fundamentals and selection of advanced fischertropsch reactors, Appl. Catal. A-Gen. 186 (1999) 55–70.

[29] I. C. Yates, C. N. Satterfield, Intrinsic kinetics of the fischer-tropsch synthesis on a cobalt catalyst, Energy Fuels 5 (1991) 168–173.

[30] A. Steynberg, M. Dry, B. Davis, B. Breman, Fischer-tropsch reactors, Stud. Surf. Sci. Catal. 152 (2004) 64– 195.

[31] R. F. Mudde, W. K. Harteveld, H. E. A. van den Akker, Uniform flow in bubble columns, Ind. Eng. Chem. Res. 48 (2009) 148–158.

12

Table 1: Mathematical model for mass and heat balance in a slurry bubble column and fixed bed. In calculation $i = CO$ or H_2 and 'nr' is number of independent reactions.

Balances	slurry bubble column	fixed bed
Mass balance for i^{th} component in large bubbles: $\frac{\partial}{\partial z}\left(\varepsilon_{large}E_{g,large}\frac{\partial C_{i,g,large}}{\partial z}\right) - \frac{\partial}{\partial z}[(U_{sg} - U_{df})C_{i,g,large}]$ $-k_{L,i,large}a_{large}(C^*_{i,large} - C_{i,L}) = 0$ $C^*_{i,large} = C_{i,g,large}/m_i$	$E_{g,large} = E_{g,large,SB}$ [27] $k_{L,i,large} = k_{L,i,large,SB}$ [20]	$E_{g,large} = 0$ $k_{L,i,large} = \infty$ $C^*_{i,large} = C_{i,L}$
Mass balance for i^{th} component in small bubbles: $\frac{\partial}{\partial z}\left(\varepsilon_{small}E_{g,small}\frac{\partial C_{i,g,small}}{\partial z}\right) - \frac{\partial}{\partial z}(U_{df}C_{i,g,small})$ $-k_{L,i,small}a_{small}(C^*_{i,small} - C_{i,L}) = 0$ $C^*_{i,small} = C_{i,g,small}/m_i$	$E_{g,small} = E_L$ [27] $k_{L,i,small} = k_{L,i,small,SB}$ [20]	$E_{g,small} = 0$ $k_{L,i,small} = \infty$ $C^*_{i,small} = C_{i,L}$
Mass balance for i^{th} component in liquid phase: $\frac{\partial}{\partial z}\left(\varepsilon_L E_L\frac{\partial C_{i,L}}{\partial z}\right) - \frac{\partial}{\partial z}(U_{ss}C_{i,L})$ $+k_{L,i,large}a_{large}(C^*_{i,large} - C_{i,L})$ $+k_{L,i,small}a_{small}(C^*_{i,small} - C_{i,L})$ $-C_s\varepsilon_L\rho_p\sum_{j=1}^{nr}R_i = 0$	$E_L = E_{L,SB}$	$E_L = 0$ $C_s\varepsilon_L = \varepsilon_{bed}$
Heat balance is derived as: $\frac{\partial}{\partial z}\left(\varepsilon_L\lambda_{ax}\frac{\partial T}{\partial z}\right) - U_{ss}\rho_s C_{ps}\frac{\partial T}{\partial z} - \alpha_{eff}a_w(T - T_c)$ $+C_s\varepsilon_L\sum_{j=1}^{nr}(-\Delta H_{Ri})R_i = 0$	$\lambda_{ax} = \lambda_{ax,SB}$ [27] $\alpha_{eff} = \alpha_{eff,SB}$ [21] $\alpha_w = \alpha_{w,SB}$	$\lambda_{ax} = 0$ $\alpha_{eff} = U_{ov}$ $\alpha_w = 4/d_{tube}$

13

Table 2: Dimensions and operating conditions.

Dimensions	SBC	FB
Diameter (m)	7.5	0.05
Height (m)	30.0	10.0
Operating conditions		
Reactor pressure (MPa)	3.0	3.0
Inlet temperature of syngas (K)	498	varies
Area of the heat transfer $(m^2/m^3 reactor)$	10.0	80.0
Slurry velocity (m/s)	0.01	-
Liquid velocity (m/s)	-	0.01
Catalyst diameter (mm)	0.05	2.0
Catalyst density (kg/m^3)	1500	1500
Catalyst hold-up $(-)$	0.25	0.6

14

Table 3: (a) Different cases in slurry bubble column model(d_p=50 μm). Note: In case 1 and 2 the $E_{L,SB}$ was calculated using Eq. (4). (b) Different cases in fixed bed model (U_{sg}=0.4 m/s).

(a) SBC			(b) FB		
Case	U_{sg} (m/s)	$E_{L,SB}(m^2/s)$	Case	d_p (mm)	U_{ov}(W/m^2/K)
1	0.3	7.77	1	2.0	400
2	0.3	1.95	2	1.0	400
3	0.4	8.52	3	2.0	1000
4	0.4	2.12	4	1.0	1000

Table 4: Productivity of the reactors.

Productivity	SBC				FB			
	Case 1	Case 2	Case 3	Case 4	Case 1	Case 2	Case 3	Case 4
$STY_{C5+}(kg/kg_{cat}/h)$	0.263	0.278	0.307	0.320	0.288	0.353	0.279	0.408
$STY'_{C5+}(kg/m^3_{G+L+cat}/h)$	99	104	115	120	259	318	251	367
$STY''_{C5+}(kg/m^3_{reactor}/h)$	97	102	112	118	161	197	156	228

Figure 1: A photo of a needle sparger used in a slurry bubble column with one-third of the needles in operation. By using long needles instead of holes, a much higher pressure drop is achieved, which leads to a much more uniform bubble size and consequently a lowered E_L.[31].
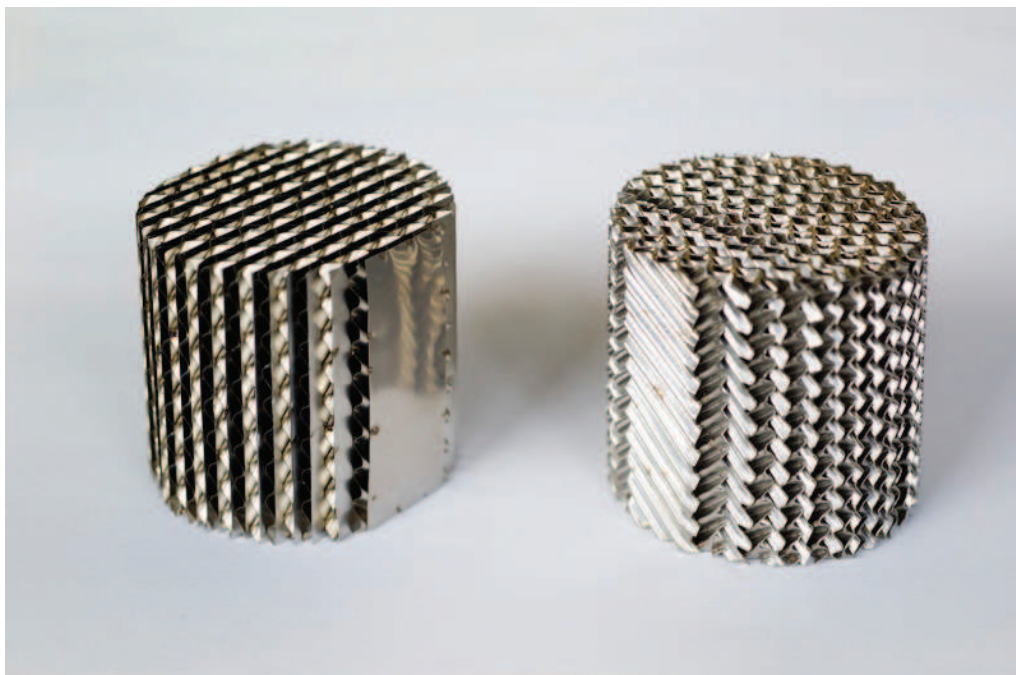
Figure 2: Photos of cross-flow structure packings used in a fixed bed reactors. By forcing the gas-liquid mixture in diagonal pathways, a much more effective radial heat transfer is obtained than in a randomly packed bed and consequently more uniform temperature profile.[5].

18
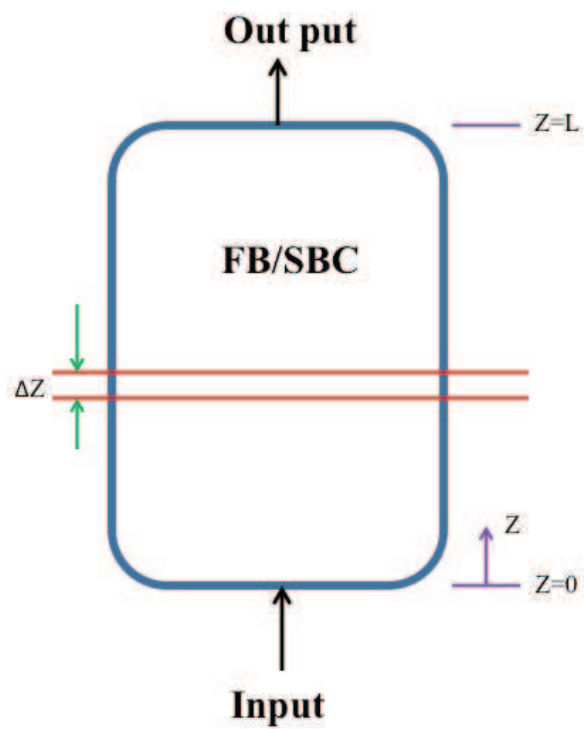
Figure 3: Schematic representation of a slurry bubble column and a fixed bed reactor model. Note: the fixed bed reactor operation is co-current, top down.
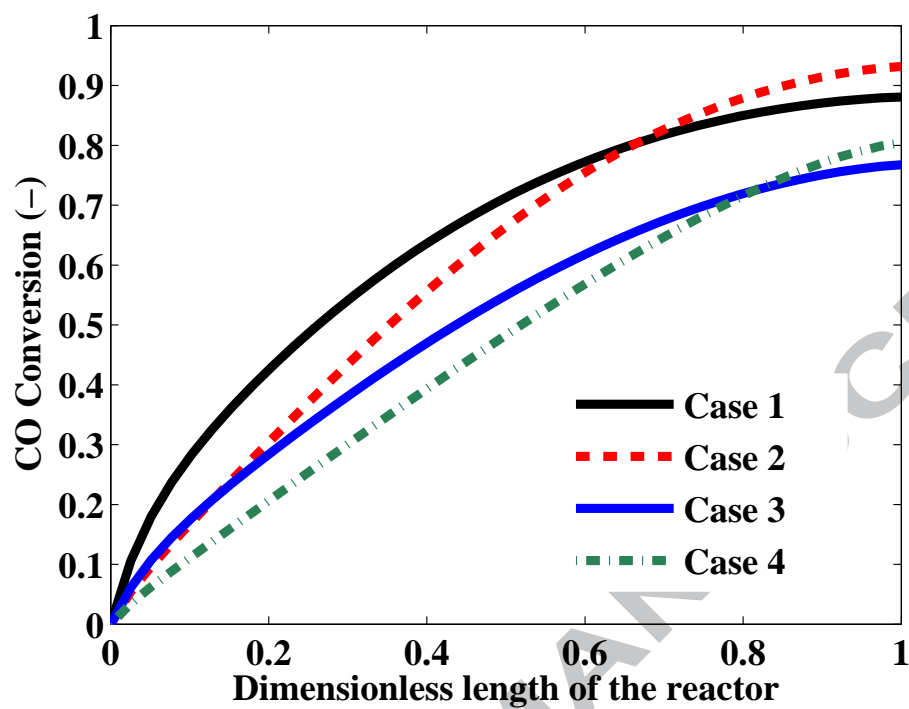
19

Figure 4: CO conversion versus dimensionless reactor length for different values of superficial gas velocities and liquid axial dispersion coefficient in a slurry bubble column with D_T=7.5m and H=30m. Note: for different cases see Table 3(a).
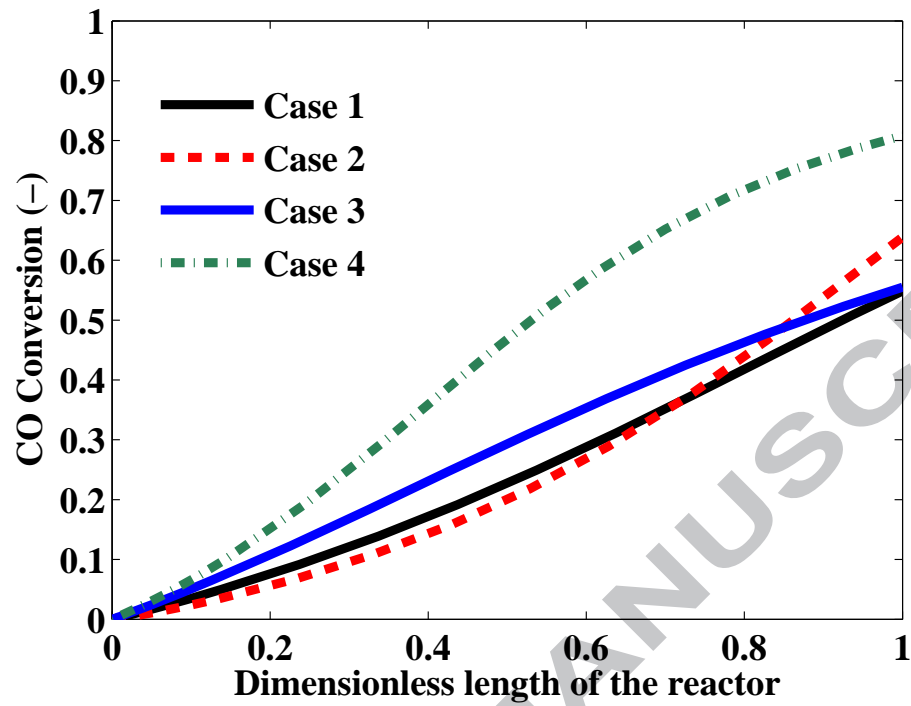
20

Figure 5: CO conversion versus dimensionless reactor length for different values of catalyst diameter and overall heat transfer values in a fixed bed reactor with $D_{T,FB}$=0.05m and H_{FB}=10m. Note: for different cases see Table 3(b).
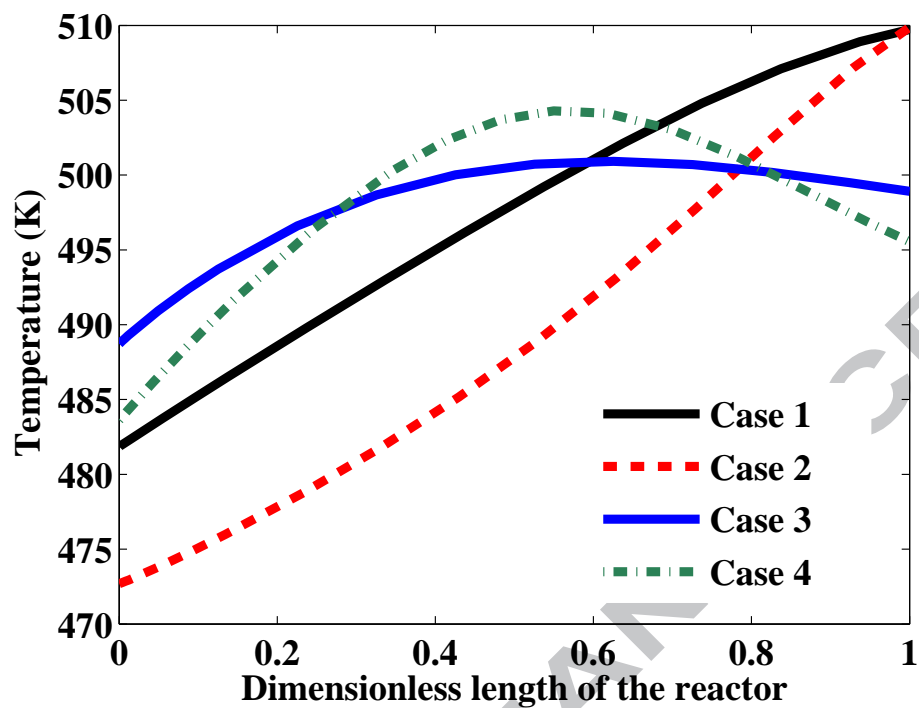
21

Figure 6: Temperature profile in the fixed bed reactor for different values of catalyst diameter and overall heat transfer values in a fixed bed reactor with $D_{T,FB}$=0.05m and H=10m. Note: for different cases see Table 3(b)
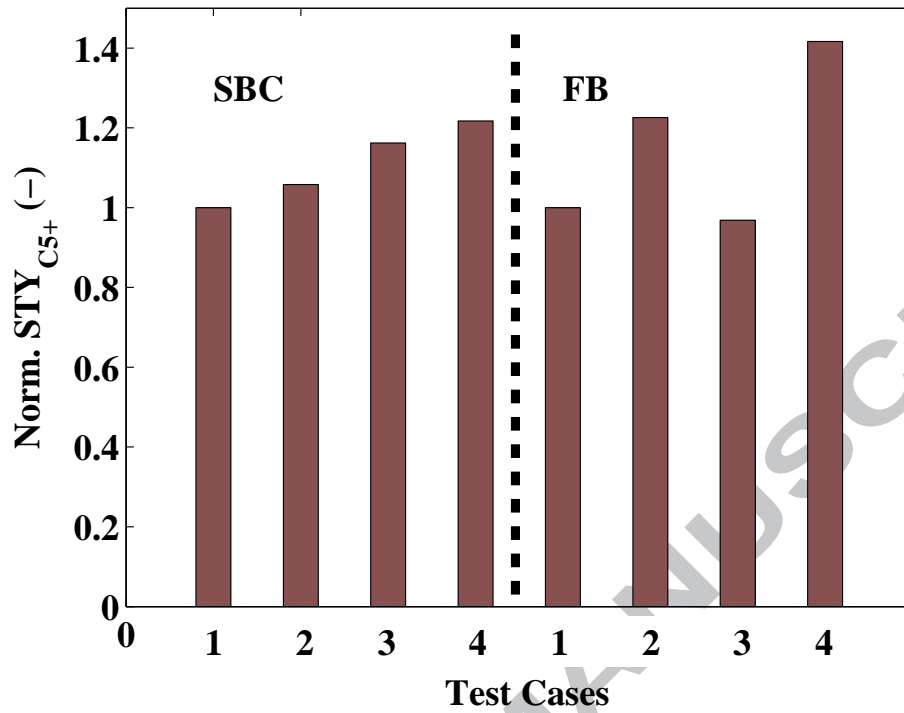
Figure 7: Normalized space time yield of a SBC and a FB reactor in an intensified operation relative to the case 1 for each reactor type.

Highlights for paper CEJ_9620

- Modelling of Fischer- Tropsch Synthesis in a fixed bed and a slurry bubble column.

- Increasing the productivity in a structured slurry bubble column by 20%.

- Improving the conversion by 40% in a fixed bed by process intensification.

- Structuring can be used to reduce reactor volume rather than increasing conversion.