Selective and Complete Catalytic Oxidation of Natural Gas in Turbulent Fluidized Beds

Jamal Chaouki[†], Danilo Klvana and Christophe Guy

Chemical Engineering Dept., Ecole Polytechnique, Montreal, Quebec, Canada
(*Received 15 December 1998 • accepted 26 April 1999*)

Abstract--Turbulent Fluidized Bed (TFB) reactors appears to be ideal for exothermic and fast reactions such as catalytic oxidation of methane. In this paper, a use of TFB reactor for two catalytic oxidation of methane: catalytic combustion of methane and catalytic selective oxidation of methane for the ethylene synthesis is described. Catalytic fluidized bed combustion of methane is shown to be an emerging technology capable of meeting all environmental constraints as far as nitrogen oxides and carbon monoxide are concerned. This reaction carried out in both the bubbling and the turbulent regimes at 450-500 °C shows that the turbulent regime is more favourable. A self-sustained combustion with complete conversion and a zero emission of NO_x and CO was achieved with a mixture of 4 % methane in air at 500 °C. The two-phase model of Werther [1990], which phenomenologically introduces the enhancement factor due to chemical reaction, predicts quite well the combustor performance. The same model but without enhancement factor (slower reactions) predicts satisfactorily the experimental data for the oxidative coupling of methane and can be used to quantify the influence of homogeneous and catalytic reactions.

Key words : Turbulent Fluidized Bed, Modelling, Catalytic Selective Oxidation, Combustion, Natural Gas

INTRODUCTION

In fluidization, as the superficial gas velocity increased, various regimes ranging from the bubbling to fast fluidization are observed. Most works in academia have been focussed on bubbling fluidized bed reactors. These reactors are described by the existence of large bubbles, a poor gas-solid contact, high gas back mixing and a low throughput and therefore, they are not suitable for fast reactions where high conversion is expected. In recent years, the fluidized bed community was mainly interested in understanding the higher velocity fluidization regimes, occurring in turbulent and circulating fluidized bed reactors. Most industrial processes now operate under turbulent regime where a more homogeneous appearance with small bubbles and a good gas-solid contact exists [Grace, 1990].

Turbulent Fluidized Beds, TFB, seems to be an ideal reactor for fast exothermic reactions at high temperatures. They offer the advantages of the exceptionally high heat transfer, intimate gas and solid contact, high overall productivity, much lower capital cost and high combustion efficiency.

Their overall homogeneous behaviour makes the gas-solid contact to become more efficient, thus enhancing the overall conversion and selectivities [Gonzalez et al., 1998; Foka, 1994]. Therefore, these reactors can provide an innovative technology for oxidizing partially or completely natural gas.

In this paper, we present experimental results obtained in TFB for 1) complete catalytic combustion of natural gas, 2) coupling oxidation of NG. On the basis of experimental results as well as on various correlations existing in the literature, we developed the same complete predictive two-phase

model with axial dispersion for these oxidative reactions. The results for the catalytic combustion for NG were presented at the first Canadian-Korean Workshop in May 1998.

TURBULENT FLUIDIZED BED HYDRODYNAMICS

1. Literature Review

The turbulent fluidization regime, which is regarded as the highly expanded gas-solid system, exists between bubbling and fast fluidization with degrees of expansion, ε, between 0.65 and 0.85. Zenz [1949] first observed this type of fluidization but Lanneau [1960] has been the first who reported the existence of turbulent fluidization. Some bubbling models are used to predict the performance of turbulent fluidized bed reactors. But such approaches generally yield erroneous results considering the fact that their descriptions are inconsistent with the physical behaviour of turbulent fluidized bed reactors where the gas superficial velocity is usually higher than a certain critical value [Bi and Grace, 1995; Cai et al., 1990]. This critical velocity, U_c, is now generally accepted as the onset of the turbulent regime. Several correlations expressed in terms of dimensionless numbers such as Reynolds, Archimedes or Froude Numbers could be used to estimate U_c (Table 1). Under this condition, solid velocity, bubble diameters and velocities are quite different from the bubbling regime [Berruti et al., 1995; Chehbouni et al., 1993, 1994]. Compared to bubbling fluidized beds, turbulent fluidized beds have upper surfaces of bed particles which are more diffuse and unclear, while the gas-solid contact efficiency and chemical conversion are higher [Massimilla, 1973; Grace and Sun, 1991; Foka et al., 1994; Chaouki et al., 1998]. Moreover, bubbling fluidized bed reactors are very sensitive to bubble behaviour which is fully responsible for the different radial and axial profiles in these reactors and it is then ex-

[†]To whom correspondence should be addressed.
E-mail : jchaouki@biopro.polymtl.ca

Table 1. Correlations for turbulent transition velocity

Reference	Correlation
Bi and Grace [1995]	A $Re_c = 0.570 Ar^{0.460}$ B $Re_c = 1.240 Ar^{0.450}$
Cai et al. [1989]	$Fr_c = (\mu/\mu_{20})^{0.2}[K \, (\rho_{g20}/\rho_g)$ $((\rho_p - \rho_g)/\rho_g) \, (D/d_p)]^{0.27}$ $K = (0.211/D^{0.27} + 2.42 \; 10^{-3}/D^{1.27})^{(1/0.27)}$
Gonzalez et al. [1995]	$Fr_c = 0.261 \, Ar^{0.10} \, [(\rho_{g20}/\rho_g)(\mu/\mu_{20})]^{0.27}$
Horio [1986]	$Re_c = 0.936 Ar^{0.472}$
Lee and Kim [1988]	$Re_c = 0.700 Ar^{0.485}$
Tsukada et al. [from Horio, 1997]	$Re_c = 0.791 Ar^{0.435}$

pected that the overall efficiency predicted by bubbling fluidized bed models for the turbulent reactors becomes very small. Therefore, these models can only be applicable to the bubbling regime where the gas superficial velocity lies between U_{mf} and U_c.

In the turbulent regime, the bubble coalescence attains an equilibrium state and the rate of bubble splitting exceeds the rate of bubble coalescence [Chehbouni et al., 1993]. Consequently, as fluidization progresses up to full scale turbulent fluidization, the bubbles become smaller and the gas-solid contact reaches maximum. Therefore, it can be concluded that the models, which are extended from bubbling fluidized bed hydrodynamics lead to the prediction of erroneous results and could not be confidently used to characterize the TFB hydrodynamics.

Hydrodynamic models, as proposed in most fluidization literature concerning turbulent fluidized bed reactors, can be classified into three groups :

• Those considering turbulent fluidized beds as homogeneous beds [Avidan, 1982; Wen 1984; Kehoe and Davidson, 1971; Van Swaij, 1978] with very small bubbles;
• Those considering two phase theory of fluidization developed originally for bubbling fluidized bed or modified two phase theory in order to predict the radial and axial profiles of suspension density [Lee and Kim, 1989; Grace, 1990; Chehbouni et al., 1993; Abed, 1994; Chaouki et al., 1998];
• Those applying the fundamental equations of fluid mechanics to model gas-solid flow structure.

2. Turbulent Fluidized Bed Modeling

These approaches suggest the use of pseudohomogeneous single phase and/or two-phase models. Single-phase models do not show difficulties in modeling, however, they impose the choice of an overall kinetic model that considers homogeneous phase and catalytic phase reactions. On the other hand, a two-phase model seems to be an interesting alternative both to separate and to simulate independently reaction effects that are important in clarifying the combustion of NG and oxidative coupling of NG reactions as well. Moreover, this model can be an excellent tool in predicting the influence of the gas phase distribution in turbulent regime (i.e. the by-pass of gas phase like bubbles through the bed) on conversion and selectivity.

Yet, only one model is available in the literature to estimate

the gas-solid phase distribution (emulsion/bubble) in the turbulent regime [Chaouki et al., 1998]. The gas fed to the reactor flows through two macroscopic regions : the dilute or bubble phase, and the emulsion phase. Exchange of gas takes place between the two phases.

It was possible to ignore temperature changes for both reactions in the TBF due to the isothermal operation. For the sake of simplicity, volume changes by reaction were also ignored (diluted reactants in the system). Moreover, physical parameters were considered constant in the axial direction. The mass balance applicable to each phase was given by :

$$\partial C_i/\partial t + U_i \partial C_i/\partial z - D_{gi}\partial^2 C_i/\partial z^2 + k_m a A_{gb}/A_{gi}(C_i - C_j) - R_i = 0 \quad (1)$$

and for steady-state operation we had

$$U_b dC_b/dz - D_{gb} d^2C_b/dz^2 + k_m a(C_b - C_e) - R_b = 0 \quad (2)$$

$$U_e dC_e/dz - D_{ge} d^2C_e/dz^2 + k_m a A_{gb}/A_{ge}(C_e - C_b) - R_e = 0 \quad (3)$$

The phases or regions were assumed to have one dimensional gas flow through them. In the case of TFB reactors, we supposed a plug flow pattern for the bubble phase and a dispersive plug flow model in the emulsion phase. The catalytic reactions took place in the emulsion and the homogeneous reaction in both phases. Therefore, considering the previous assumptions, the following set of equations in dimensionless form was obtained for each component.

$$d\psi_b/d\lambda + N_b(\psi_b - \psi_e) - (H/(U_b C_0))R_b = 0 \quad (4)$$

$$d\psi_e/d\lambda - 1/Pe_e d^2\psi_b/d\lambda^2 + N_e/\beta^2(\psi_b - \psi_e) - (H/(\beta U_e C_0))R_e = 0 \quad (5)$$

3. Hydrodynamic Parameter

Foka et al. [1996] evaluated the interphase mass transfer ($k_m a$) in bubbling and turbulent regime by using RTD techniques with radioactive tracers and employing the two-phase model proposed by van Deemter [1961]. In addition, these authors have studied particle size, reactor diameter, and temperature effects. They proposed the following correlation to estimate the interphase mass transfer.

$$k_m a = U/0.613 \; Sc^{0.37} \quad (6)$$

The effective axial gas dispersion coefficient was evaluated according to a correlation proposed by Foka et al. [1996].

$$Pe_z = 7.10^{-2} Ar^{0.32}(d_p/D)^{-0.4} \quad (7)$$

Finally, the β ratio was calculated by using Eq. (8) [Chaouki et al., 1998].

$$\beta_r = (\varepsilon_{mf} + k_e(U - U_{mf}))/(\varepsilon_{b\infty}(1 - \exp(-k_b(U - U_{mf}))))^{(1 + (r/R)2 + 3(r/R)11)} \quad (8)$$

CATALYTIC COMBUSTION OF NATURAL GAS

1. Kinetic Parameter

An industrial reforming catalyst (Pt-Sn/Al$_2$O$_3$) with a very low platinum content (0.2 %) and doped with tin was used for this
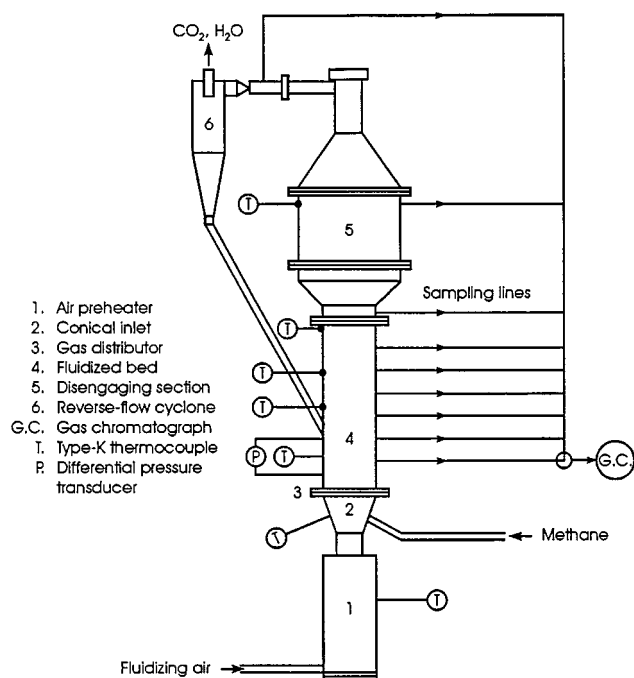
Fig. 1. Schematic diagram of experimental combustor (100 mm I.D.).

1. Air preheater
2. Conical inlet
3. Gas distributor
4. Fluidized bed
5. Disengaging section
6. Reverse-flow cyclone
G.C. Gas chromatograph
T. Type-K thermocouple
P. Differential pressure transducer

Fig. 2. Experimental and predicted conversions for catalytic combustion of methane.

reaction. The kinetic study was carried out in a tubular fixed bed reactor with a gas mixture containing 3 % of methane in air and is detailed elsewhere [Chaouki et al., 1994]. The ignition temperature was around 275 °C. Since the study used an excess of air, the rate of combustion in terms of the concentration of methane was expressed as :

$$R_{CH4} = k_0 \exp(-E/RT) C_{CH4} \tag{9}$$

where k_0 is evaluated to be (2×10^8) and E/R to be 11,100 K.

2. Experimental Setup and Procedure

A small pilot scale reactor of 100 mm I.D. was used for this reaction (Fig. 1). It was equipped for the sampling and analysis of reaction products. The probes were connected to a gas chromatograph. An electric resistance of 6 kW preheated the inlet gas. The catalyst mean diameter was 200 μm. The minimum fluidization void fraction ε_{mf} was 0.48 and the bulk density 570 kg/m³. An initial bed height H_0 of 2D was used in all experiments. A gas mixture of 3 % methane in air was premixed in the reactor plenum using steel filings and was used in a series of experiments at three different temperatures (450, 475 and 500 °C) and at two velocities 0.77 and 1.1 m/s, in the bubbling and turbulent regimes respectively.

3. Modeling the Experiments

As shown in Fig. 2, the two-phase model obtained at the conditions of the reaction experiments gives a poor prediction of the conversion. This is normal since this model is valid only when the mass-transfer rate is not influenced by the reaction rate [Van Swaij and Zuiderweg, 1973; Werther, 1980] i.e. for k<1-2 s⁻¹ whereas the rate constant of the catalyst used here is of the order of 70 s⁻¹.
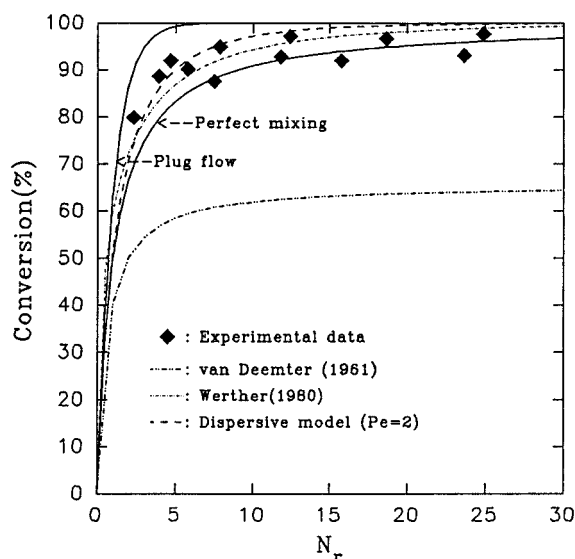
Under these conditions a chemical acceleration factor can

be phenomenologically introduced. The most appropriate two-phase model to industrial scale fluid bed reactors is the model of Werther [1980]. This model introduces the film theory :

$$C/C_0 = \exp(Ha\,N) \tag{10}$$

Where Ha is the Hatta number.

The Eq. (10) is valid only for Ha > 1. The Hatta number estimated from our experiments was above 1 and Eq. (10) was used to model the reaction. It is clear from the Fig. 2 that this model can satisfactory predicts our data in a wide range of the number of reaction units, N_r.

4. Self-sustained Combustion

In the bubbling regime, a mixture of 4 % of NG in air was used and above 500 °C the conversion was 100 %. The system operated at 0.75-0.8 m/s and the maximum temperature was 540 °C. No NO$_x$ and no carbon monoxide were recorded with a LandCombus device (sensitivity 1 ppm). At these conditions 2.9 kW were produced by the reaction and were able to sustain the reacting system. The ratio of the power required to raise the temperature of the gas mixture to the power generated by the reaction was 0.077 and 0.074 in the bubbling and turbulent beds respectively. Moreover in the turbulent regime, a power of 4.6 kW was generated and no pollutants were recorded. The system was operated at 1.1 to 1.8 m/s using a mixture of 4 % of methane in air.

It is clear from these experiments that in the turbulent regime the power generated by the reaction is higher than in the bubbling regime.

The parameters obtained in this study were used to estimate the optimal operating conditions and the bed diameter of a combustor that could generate 50 kW. Typically, with an inlet mixture containing 5 % of methane in air, an initial bed height of 2D, and when the gas velocity is 1.5 m/s, a minimum bed diameter of 240 mm is required at a temperature of 500 °C to achieve a complete combustion.
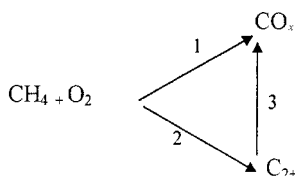
Table 2. Kinetic parameters for the oxidative coupling of methane [Al-Zahrani et al., 1994; Mleczko et al., 1990]

$R_i = k_i(P_{O2})^m(P_{CH4})^n (P_{CO2})^\gamma$ (mol/g/min)
$R_{COx} = k_i(P_{O2})^{0.92}(P_{CH4})^{0.46} (P_{CO2})^{-0.69}$
$R_{C2+} = k_i(P_{O2})^{0.27}(P_{CH4})^{0.68}(P_{CO2})^{-0.44}$
$R_{CH4} = k_i(P_{O2})^{0.33}(P_{CH4})^{0.65}(P_{CO2})^{-0.46}$
$R_{C2+ \to COx} = k_i(P_{O2}) (P_{C2+})$

$k_i = A_o \exp(-E_o/RT)$ (mole/g/min/atm$^{m+n+\gamma}$)		
Component i	E_o (kcal/mol)	A_o (mol/g/min/atm$^{m+n+\gamma}$)
CO_x	58.6	6.565e6
C_{2+}	61.5	1.825e8
CH_4	61.0	3.265e8
$C_{2+} \to CO_x$	56.0	2.087e10

COUPLING OXIDATION OF NATURAL GAS

1. Kinetic Parameter

Complex mechanisms and reactions in homogeneous and catalytic phases characterize the ethylene synthesis by catalytic partial oxidation of natural gas. We have adopted a global mechanism assuming a triangular path scheme.

$$CH_4 + O_2 \begin{array}{c} \nearrow^{1} CO_x \\ \searrow_{2} \quad \downarrow 3 \\ \qquad C_{2+} \end{array}$$
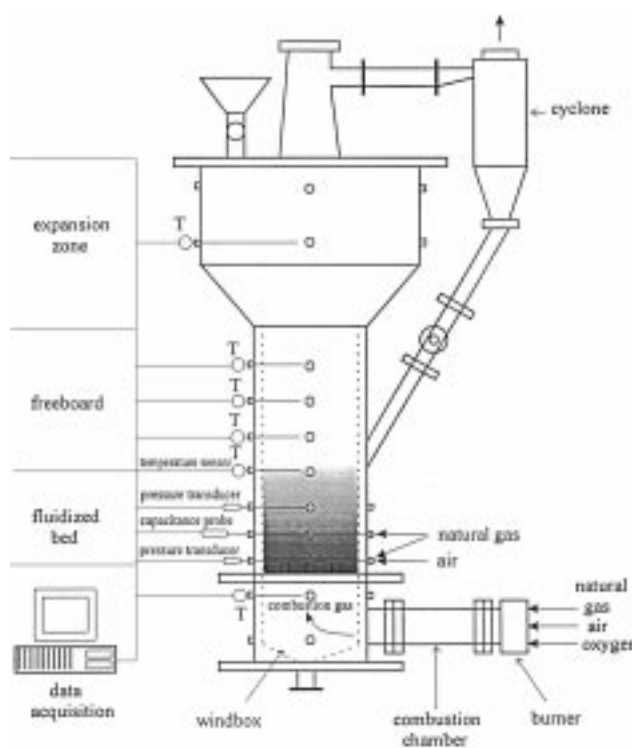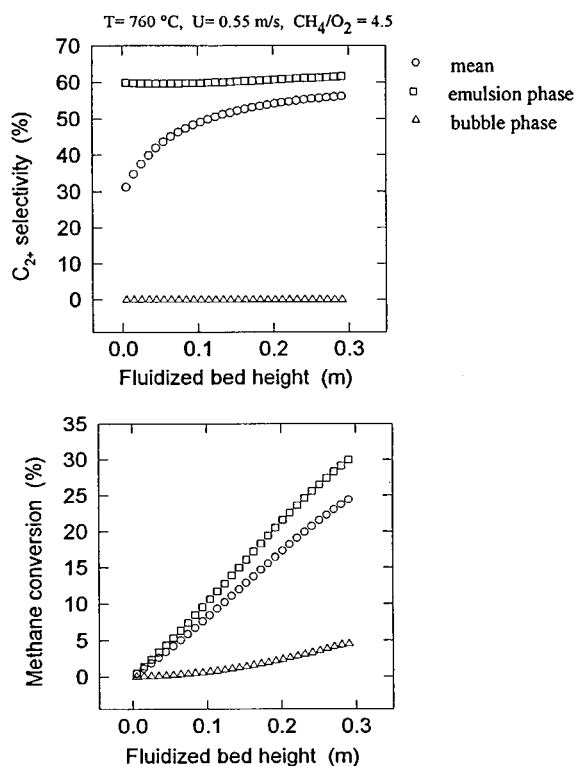
The kinetic parameters for the catalytic oxidation of methane were estimated by using data from Al-Zahrani et al. [1994] and power law models. Furthermore, the C_{2+} oxidation reaction rate was assumed considering the kinetic parameters suggested by Mleczko et al. [1990]. Kinetic constants and models are summarized in Table 2.

2. Experimental Setup and Procedure

The hydrodynamic and reaction experiments were carried out in a pilot TBF unit (0.2 m ID) used. Schema of this pilot reactor is shown in Fig. 3. The fluidized bed zone was 0.5 m high with a cap distributor. A burner (counter-rotation type) using natural gas and air, or air mixed with oxygen heated and controlled bed temperature. Reactants (natural gas and air) were fed through the sidewalls into the bed through perforated tube distributors. The reactor was also equipped the sampling and gas chromatographic analysis, pressure and temperature measurements. A capacitance probe was employed to measure voidage profiles in the radial and axial directions in the bed. A data acquisition system was used to record continuously signals of thermocouples, pressure transducers, and capacitance probes. A more detailed description of the equipment was reported elsewhere [Chaouki et al., 1998]. The catalyst used was MgO with a mean diameter 120 μm.

3. Modeling the Experiments

Fig. 4 shows the predicted methane conversion and C_{2+} selectivity respectively with a two-phase model. Evidently, methane

Fig. 3. Schematic diagram of experimental pilot TFB reactor for the coupling oxidation of methane (200 mm I.D.).

Fig. 4. Prediction of conversion and selectivity with two-phase model.

conversion and selectivity were important in the emulsion phase because the catalytic reaction and gas flowrate were favoured in this phase. Also, in the bubble phase, they were completely
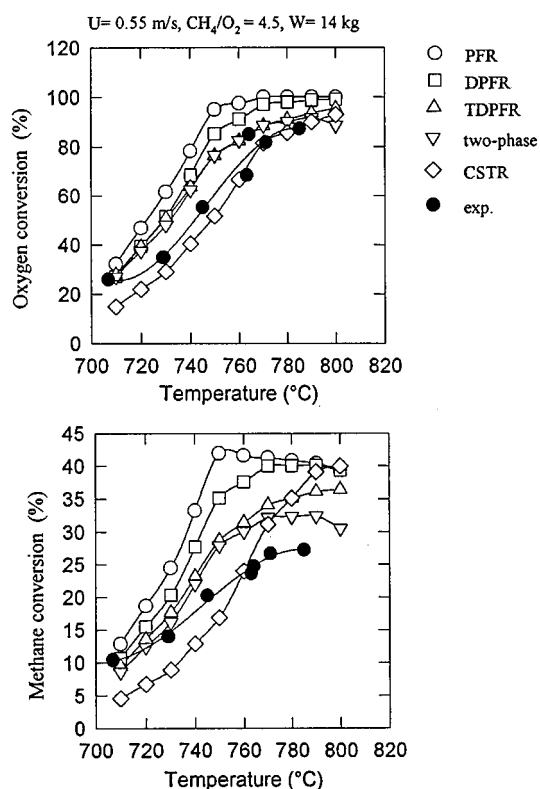
U= 0.55 m/s, CH$_4$/O$_2$= 4.5, W= 14 kg

Fig. 5. Effect of temperature on the oxygen and methane conversions for the coupling oxidation of methane.

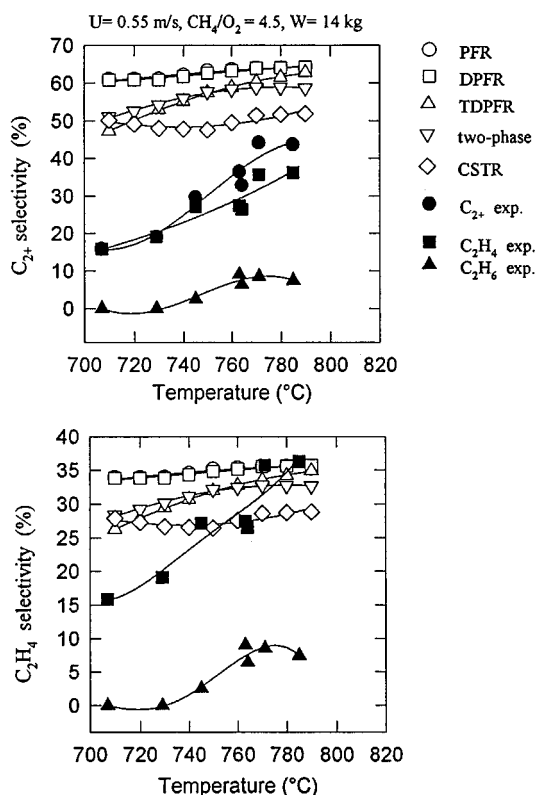U= 0.55 m/s, CH$_4$/O$_2$= 4.5, W= 14 kg

Fig. 6. Effect of temperature on C$_2$H$_4$ and C$_2^+$ selectivities for the coupling oxidation of methane.

oxidized to and consequently the mean values of these variables in the bed were less than those obtained in the emulsion phase.

The experimental and predicted conversions and selectivities considering different pseudohomogeneous models and the above two-phase model are illustrated in Figs. 5 and 6. Pseudohomogeneous models considering two-dimensional dispersive plug flow with radial voidage model (TDPFR), continuous stirred-tank model (CSTR), plug flow model (PFR) and dispersive plug flow model (DPFR) were analyzed in previous work [Chaouki et al., 1998]. The two-phase model predicted reasonably well the experimental data for methane conversion, ethylene selectivity and overestimated slightly the oxygen conversion. However, selectivity was overestimated.

CONCLUSION

The general two-phase model was adapted to hydrodynamic turbulent regime and used to simulate catalytic combustion of methane and the ethylene synthesis by methane oxidative coupling in a TFB reactor operating with a co-feed approach.

A combustion process was implemented using a TFB. This combustion was carried out with 4 % methane in air for self-sustained experiments. The two-phase model of Werther, which phenomenologically introduces the enhancement factor due to chemical reaction, predicts quite well the reactor performance. Typically, to generate 50 kW, a minimum bed diameter of 240 mm is required at a temperature of 500 °C.

For ethylene synthesis by methane oxidative coupling in a TFB reactor, a two-phase model was also adapted. It predicts satisfactorily the experimental data and can be used to explain the influence of homogeneous and catalytic reaction for the oxidative coupling of methane.

NOMENCLATURE

a   : surface mass transfer [m^2/m^3]
Ar   : Archimede number [$\rho_g d_p^3 g (\rho_P-\rho_g)/\mu^2$]
A$_{ge}$: gas surface hold up in emulsion phase [m^2]
A$_{gb}$: gas surface hold up in bubble phase [m^2]
A$_{gi}$: gas surface hold up in i phase [m^2]
C$_o$: inlet composition [mol/m^3]
C$_i$: concentration in phase i [mol/m^3]
C$_b$: concentration in bubbling phase [mol/m^3]
C$_e$: concentration in emulsion phase [mol/m^3]
C$_{CH4}$: methane concentration [mol/m^3]
d$_p$: average particle diameter [m]
D   : reactor diameter [m]
D$_g$: gas phase dispersion coefficient [m^2/s]
D$_{gi}$: gas phase dispersion coefficient in phase i [m^2/s]
D$_{gb}$: gas phase dispersion coefficient in bubbling phase [m^2/s]
D$_{ge}$: gas phase dispersion coefficient in emulsion phase [m^2/s]
D$_v$: component gas diffusivity [m^2/s]
E   : activation energy [kJ/mol]
Fr   : Froude number [U/(gD)$^{0.5}$]
H   : height of fluidized bed]m]
Ha   : Hatta number [(k D$_v$)/k$_m$]
k   : kinetic constant [s^{-1}]
k$_b$: parameter of Eq. (3)
k$_e$: parameter of Eq. (2)

k_m : interphase mass transfer coefficient [m/s]
N : $k_m aH/U$
N_e : interphase mass transfer rate/convective emulsion phase rate [$k_m aH/U_e$]
N_b : interphase mass transfer rate/convective bubble phase rate [$k_m aH/U_b$]
N_r : number of reaction units [$\beta kH/U$]
Pe_e : emulsion Peclet number [$U_e H/D_{ge}$]
R : reactor radius [m]
R_i : overall reaction rate in phase i [$\sum r_{ij}$]
R_b : overall reaction rate in bubble phase [$\sum r_{ij}$]
R_e : overall reaction rate in emulsion phase [$\sum r_{ij}$]
Re : Reynolds number [$\rho_g d_p U/\mu$]
r : radial coordinate [m]
r_j : reaction rate [mol/s·kg]
r/R : dimensionless radius
Sc : Schmidt number [$\mu/\rho_g Dv$]
U : gas superficial velocity [m/s]
U_c : onset of the turbulent regime [m/s]
U_{mf} : minimum fluidization velocity [m/s]
T : temperature [K]
w : weight of catalyst [kg]
z : axial coordinate [m]

Greek Letters

β : interphase ratio [$A_{ge}/A_{gb} = \varepsilon_e/\varepsilon_b$]
β_{r0} : interphase ratio at center of the bed
β_r : radial interphase ratio
ρ_g : gas phase density [kg/m^3]
ρ_p : particle density [kg/m^3]
ε_b : bubble phase voidage
ε_{bc} : bubble phase voidage at the onset of turbulent regime
ε_e : emulsion bed voidage
ε_m : mean bed voidage
ε_{mf} : voidage at minimum fluidization
$\varepsilon_{b\infty}$: parameter of Eq. (3)
μ : gas phase viscosity [kg/m·s]
λ : dimensionless bed height [z/H]
ψ_j : mol/volume composition ratio [C_j/C_0]

REFERENCES

Abed, R., "Fluidization," Kunii, D., et Toei, R. eds., Engineering Foundation, **137**, 7 (1994).

Al-Zahrani, S., Song, Q. and Lobban, L., "Effects of CO$_2$ during Oxidative Coupling of Methane over Li/MgO : Mechanisms and Models," *Ind. Eng. Chem. Res.*, **33**, 251 (1994).

Avidan, A., "Turbulent Fluid Bed Reactors using Fine Powder Catalysts," AIChE-CIESC *Mtg* Beijing, 411 (1982).

Berruti F., Chaouki, J., Godfroy, L., Pugsley, T. S. and Patience, G. S., "Hydrodynamics of Circulating Fluidized Bed Risers : a Review," *Can. J. Chem.*, **73**, 579 (1995).

Bi, H. T. and Grace, J. R., "Effect of Measurement Method on the Velocities Used to Demarcate the Onset of Turbulent Fluidization," *Chem. Eng. J.*, **57**, 261 (1995).

Cai, P., Jin, Y., Yu, Z. Q. and Wang, Z. W., "Mechanism of Flow Regime Transition from Bubbling to Turbulent Fluidization,"

AIChE J., **36**, 955 (1990).

Chaouki, J., Guy, C., Sapunzhiev, C. and Klvana, D., "Combustion of Methane in a Cyclic Catalytic Reactor," *Ind. Eng. Chem. Res.*, **33**, 2957 (1994).

Chaouki, J., Gonzalez, A., Guy, C. and Klvana D., "Two-Phase Model for a Catalytic Turbulent Fluidized Bed Reactor : Application to Ethylene Synthesis," *Chem. Eng. Sci.*, accepted (1999).

Chehbouni, A., Chaouki, J., Guy, C. and Klvana, D., "Characterization of the Flow Transition between Bubbling and Turbulent Fluidization," *Ind. Eng. Chem. Res.*, **3**, 324 (1994).

Chehbouni, A., Chaouki, J., Guy, C. and Klvana, D., "Effets de différents paramètres sur la vitesse de transition de la fluidisation en régime turbulent," *Can. J. Chem. Eng.*, **4**, 134 (1993).

Davidson, J. F. and Harrison, D., "Fluidization," Cambridge University Press, New York (1963).

Foka, M., Chaouki, J., Guy, C. and Klvana, D., "Gas Phase Hydrodynamics of a Gas-Solid Fluidized Bed," *Chem. Eng. Sci.*, **51**(5), 713 (1996).

Foka, M., Chaouki, J., Guy, C. and Klvana, D., "Natural Gas Combustion in a Catalytic Turbulent Fluidized Bed," *Chem. Eng. Sci.*, **49**(24), 4269 (1994).

Grace, J. R. and Sun, G., "Influence of Particle Size Distribution on the Performance of Fluidized Bed Reactors," *Can. J. Chem. Eng.*, **69**, 1126 (1991).

Grace, J. R., "High Velocity Fluidized Beds Reactors," *Chem. Eng. Sci.*, **45**(8), 1953 (1990).

Horio, M., "Hydrodynamics," in Circulating Fluidized Beds, ed. Grace, J. R., Avidan, A. A. and Knowlton, T. M., Blackie Academic & Professional, London 1-21-85 (1997).

Horio, M., "The Onset of Turbulent Fluidized Beds," *J. Soc. Powder Tech. Japan*, **23**, 20 (1986).

Kehoe, P. W. K. and Davidson, J. F., "Continuously Slugging Fluidized Beds," *Instn. Chem. Engrs. Sym. Ser.*, **33**, 97 (1971).

Lanneau, K. P., "Gas-solids Contacting in Fluidized Bed," *Trans IChemE*, **38**, 125 (1960).

Lee, G. S. and Kim, S. D., "Gas Mixing in Slugging and Turbulent Fluidized Beds," *Chem. Eng. Comm.*, **86**, 91 (1989).

Massimilla, L., "Behavior of Catalytic Beds of Fine Particles at High Gas Velocities," *AIChE Symp Ser*, **69**, 11 (1973).

Massimilla, L., "In Fluidization," 2nd edition Academic Press, New York (1985)

May, W. G., "Fluidized Bed Reactor Studies," *Chem. Eng. Progr.*, **55**, 49 (1959).

Miwa, K., Mori, S., Kato, T. and Muchi, I., "Mixing and Contacting in Gas-Solid Fluidized Beds," *Chem. Eng.*, **12**, 187 (1972).

Mleczko, L., Andorf, R. and Baerns, M., "Prediction of the Performance of a Fluidized Bed Reactor for the Catalytic Oxidative Methane Coupling to C$_2$ Hydrocarbons," AICHE Annual Meeting, Nov. 11-16, Chicago (1990).

Mori, S. and Wen, C. Y., "Estimation of Bubble Diameter in Gaseous Fluidized Beds," *AIChE J.*, **20**, 109 (1975).

Rowe, P. N. and MacGillivray, H. J., In "Fluidization," Edited by Grace, J. R. and Matsen J. M., New York, 545 (1980).

Van Deemter, J. J., "Mixing Patterns in Large-scale Fluidized Beds," *Chem. Eng. Sci.*, **13**, 143 (1961).

Van Swaij, V. P. M. and Zuiderweg, F. J., Proc. Inter. Symp. on Fluidization and Its Applications. Edited by Cepadues, Tou-

louse, France, 454 (1973).

Van Swaij, V. P. M., "The Design of Gas-solids Fluid Bed and Related Reactor," *ACS Symp Ser.*, **72**, 193 (1978).

Wen, C. Y., "Chemical Reaction in Fluidized Beds," In Recent Advances in the Engineering Analysis of Chemically Reacting Systems,"Edited by Doraisamy, L. K., Wiler Eastern, New Delhi, 256 (1984).

Werther, J., "Mathematical Modeling of Fluidized Bed Reactors," *Intern. Chem. Eng.*, **20**(4), 529 (1980).

Zenz, F. A., "Two Phase Fluid-Solid Flow," *Ind. Eng. Chem.*, **41**, 2801 (1949).

Zhang, W., Tung, Y. and Johnson, F., "Radial Voidage Profiles in Fast Fluidized Beds of Differents Diameters,"*Chem. Eng. Sci.*, **46**, 3045 (1991).