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Chemical Engineering Journal 137 (2008) 681–685

Chemical Engineering Journal

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Mathematical modeling of the continuous process for synthesis of nanofibrous carbon in a moving catalyst bed reactor with recirculating gas flow

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Received 5 May 2007; received in revised form 26 June 2007; accepted 29 June 2007

Abstract

A continuous process for synthesis of nanofibrous carbon from methane in a reactor with a moving bed of the Ni–Al_2O_3 catalyst (90 wt.% Ni) and intensively recirculated gas flow is considered. Dependencies for calculating outlet characteristics of the gas mixture and catalyst are suggested. Comparison of various types of continuous reactors shows that the suggested reactor is preferable.

Keywords: Nanofibrous carbon; Filamentous carbon; Methane decomposition; Ni–Al_2O_3 catalyst; Reactor; Moving catalyst bed; Gas recirculation

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1. Introduction

Nanofibrous carbon (NFC) is a kind of carbon materials with fibers of 1–150 nm diameter, the fibers being synthesized through hydrocarbon decomposition and CO disproportionation over VIII group metals [1–3]. Depending on the catalyst used, gas mixture compositions and temperature, carbon fibers of three modifications can be produced. These are: multilayer carbon nanotubes (basal planes are deformed into nested cylinders in parallel to the fiber axis), fibers with basal planes perpendicular to the fiber axis, and fibers with planes deformed into nested cones at an angle to the fiber axis. Numerous studies of NFC properties have revealed their potentialities in a number of areas. They can be used as unique sorbents, catalysts, catalyst supports, biologically active substances, electrodes, fillers in electroconductive plastics and dyes, etc. [2,4–10]. A number of companies are engaged in large-scale production of nanofibrous carbon (see Ref. [11] for description of the producers and NFC types). The overwhelming majority of the producers employ batch reactors but only few of them use continuous processes [11–15]. These are, for example, a horizontal tube reactor with a moving fluidized catalyst bed and gas counterflow [11,14], a top-open vertical conical reactor where the catalyst is made bottom-up moving but the gas is fed top-down [12], and a tilted rotating tube reactor [13]. Problems of mathematical modeling of batch [16–18] and continuous [15,19–20] processes are discussed in some papers. Nevertheless, the choice of optimal reactor type and operation mode for the continuous process remains as yet an urgent problem.

Natural gas consisting mainly of methane is most abundant and inexpensive feedstock for synthesis of nanofibrous carbon. Nickel is the most active catalyst for the process among the VIII group metals. The currently available high-nickel catalysts [21–24] allow the nanofibrous carbon to be synthesized in the form of mesoporous granules with 1–5 mm diameter and carbon content up to 99.7% [25,26]. Fig. 1 shows an electron micrograph and a schematic of an individual fiber of the granule [27]. Natural and oil associated gases were proposed [25,28] to use as the feedstock for synthesis of granulated NFC. The process of NFC synthesis from methane and natural gas is implemented on the scale of a batch fluidized bed reactor, the capacity for NFC being 0.5 kg [25] and 2.4 kg [29] per one operation cycle.

For the high-nickel catalyst (90 wt.% Ni–AlO_3) [21], the kinetics of the formation of nanofibrous carbon from a CH_4–H_2 mixture at ambient pressure has been studied [27] and a mathematical model including catalyst deactivation has been proposed for the observed process kinetics [16]. The suggested mathematical model has been used for calculating the batch processes in

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doi:10.1016/j.cej.2007.06.036

Nomenclature

a	relative activity of the catalyst
c	specific carbon content of the catalyst (kg/kg)
c_1	specific carbon content of the catalyst at the reactor outlet (kg/kg)
c_m	maximal specific carbon content on the catalyst (kg/kg)
j_c	specific flow rate of carbon in methane feedstock (kg/h kg)
J_c	flow rate of carbon in methane feedstock (kg/h)
j_k	specific flow rate of catalyst (kg/h kg)
J_k	flow rate of catalyst (kg/h)
k	coefficient depending on temperature (kg/h kg bar)
k_a	coefficient depending on temperature (h)
k_H	coefficient depending on temperature (bar$^{-0.5}$)
K_p	equilibrium constant (bar)
m_0	catalyst mass in the reactor (kg)
p_{CH_4}	partial pressure of methane (bar)
p_{H_2}	partial pressure of hydrogen (bar)
P	pressure of the gas mixture (bar)
q	specific gas flow rate (m^3/h kg)
Q	methane flow rate (m^3/h at standard conditions)
r_m	maximal specific rate of carbon formation (kg/h kg)
R	universal gas constant (J/mol K)
t	time (h)
T	temperature (K)
x	methane conversion
Greek letter	
τ	catalyst contact time (h)

various type reactors to show that the highest carbon yield (carbon content per unit mass of the catalyst after its deactivation) is achieved, at otherwise identical conditions, in a reactor with ideal catalyst and gas mixing [16,17]. It is reasonable to suppose that employing reactors with ideal catalyst and gas mixing in continuous processes can allow the highest carbon yield to be achieved, too. The process conducted in such a reactor with selective withdrawal of the carbonized particles is considered elsewhere [19]. However, it is very difficult in practice to provide the selective withdrawal of the fully deactivated particles. It seems simpler to use a moving catalyst bed reactor with recirculating gas flow as a kind of the continuous reactor. The present work is aimed at derivation of computational dependencies and at mathematical modeling of the process as applied for synthesis of nanofibrous carbon from methane catalyzed by Ni–Al_2O_3 (90 wt.% Ni).

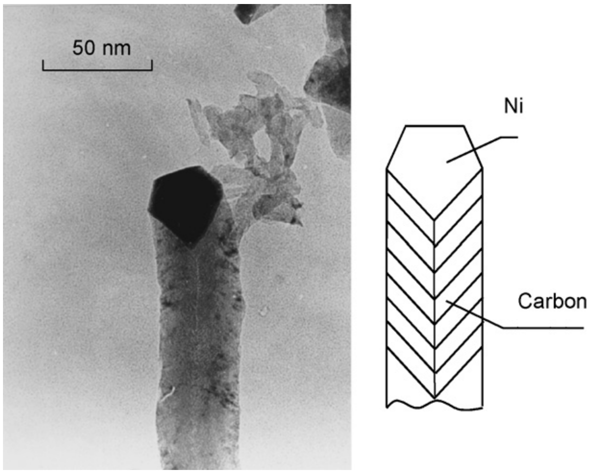

Fig. 1. Nanofibrous carbon on nickel-containing catalyst [27].

2. The kinetic model of formation of nanofibrous carbon from a CH_4–H_2 mixture over a high-loaded nickel catalyst and experimental

The mathematical model of the formation of NFC from a methane–hydrogen mixture at atmospheric pressure including catalyst deactivation [16] was the basis of calculating the process in the reactor.

In terms of this model, the catalyst state at every instant is characterized by two quantities, i.e. by the quantity of carbon formed per 1 g of catalyst, c (g/g), and the relative catalyst activity, a, changing from 0 to 1. The catalyst deactivation is considered as a decrease in the relative activity caused by the carbon deposition on the surface. The catalyst is considered fully deactivated when the relative activity drops down to zero. The following equations are suggested for the process description:

$$\frac{dc}{dt} = r_m a, \tag{1}$$

$$\frac{da}{dt} = -k_a r_m^2 c a, \tag{2}$$

where t is time (h), r_m is the maximal specific rate of carbon formation depending on the gas mixture composition and temperature (g/h g),

$$r_m = k\frac{p_{CH_4} - p_{H_2}^2/K_p}{(1 + k_H\sqrt{p_{H_2}})^2}, \tag{3}$$

p_{CH_4}, p_{H_2} are partial pressures of methane and hydrogen (bar), respectively, k_a, k, K_p, k_H are coefficients depending on temperature as follows:

$$k_a = \exp\left(\frac{135600}{RT} - 32.077\right), \tag{4}$$

$$k = \exp\left(20.492 - \frac{104200}{RT}\right), \tag{5}$$

$$K_p = 5.088 \times 10^5 \exp\left(-\frac{9.12 \times 10^4}{RT}\right), \tag{6}$$

$$k_H = \exp\left(\frac{163200}{RT} - 22.426\right), \tag{7}$$

R is the universal gas constant (J/(mol K)).

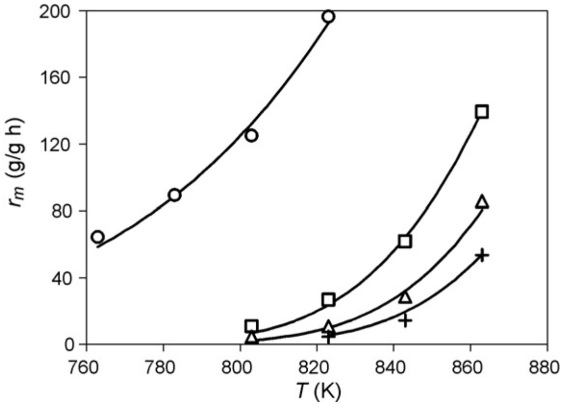

Fig. 2. Comparison of calculated data (lines) and experimental data (points) on temperature dependence of the rate of carbon formation at different hydrogen volume fractions: 0% (◯), 15% (□), 30% (△), 40% (+).

The model is formulated based on analysis of experimental kinetic data [27] obtained at atmospheric pressure, temperature of 763–863 K and hydrogen proportion of 0–40 vol% in the methane–hydrogen mixture. It is presumed that the process limiting stage is the decomposition of methane into carbon and hydrogen:

$$CH_4 = C + 2H_2, \tag{8}$$

while the cleavage of the first hydrogen atom from a methane molecule adsorbed by the catalyst surface is the limiting stage in the mechanism of reaction (8). The deactivation equation is derived based on the phenomenological approach.

The calculated data obtained with dependence (3) and the experimental data are compared in Fig. 2.

The case of carbon formation on the catalyst particles at constant composition of the gas phase (p_{CH_4} = constant, p_{H_2} = constant) is a spectacular illustration of specific features of the process kinetics. In this case, the time-dependent carbon loading on the catalyst tends asymptotically to the maximal quantity c_m which increases with a decrease in temperature and an increase in hydrogen concentration in the mixture. Integration of equation system (1)–(2) at the starting conditions $c = 0$ and $a = 1$ at $t = 0$ gives the following dependence of specific carbon loading on time:

$$c = c_m \text{th}\left(\frac{r_m}{c_m}t\right), \tag{9}$$

where

$$c_m = \sqrt{\frac{2}{k_a r_m}}. \tag{10}$$

Comparative experimental and calculated data on the time dependence of specific carbon yield (9) are plotted in dimensionless coordinates in Fig. 3.

3. The problem formulation and derivation of equations

Under consideration is a moving bed reactor with recirculating gas flow. Fig. 4 is a simplified schematic of the reactor; flow directions are indicated. A catalyst and methane are fed from the left; their flow rates are J_k (kg/h) and Q (m^3/h at standard conditions), respectively. The carbonized catalyst and the methane–hydrogen mixture are removed to the right. The gas recirculation ratio is set large enough to approach the regime of ideal mixing the gas phase and to provide approximately constant gas content and temperature inside the reactor. The reactor volume is chosen to allow the catalyst mass to be m_0 (kg). In addition, the formulation of the mathematical model is based on the following assumptions:

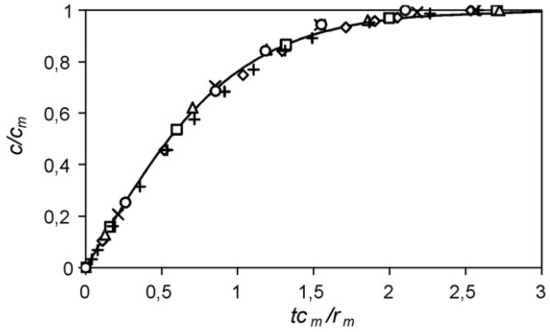

Fig. 3. Experimental (points) and calculated (lines) dependencies of dimensionless carbon content on the catalyst on dimensionless time at different temperatures and compositions of the reaction medium: 803 K 0% H_2 (◊), 823 K 0% H_2 (□), 843 K 0% H_2 (△), 863 K 0% H_2 (×), 823 K 15% H_2 (+), 843 K 15% H_2 (◯).

- The particle size and thickness of the catalyst bed are small enough to allow ignoring the internal and external diffusion resistance and considering the process to occur in the kinetic region.
- The catalyst moves but is not mixed, and its parameters depend only on the longitudinal coordinate of the reaction (one-dimensional model).
- This is a stationary process at temperature T and pressure P.

We need to determine the outlet characteristics of the catalyst and gas.

An outlet characteristic of the catalyst is the specific carbon content, c_1, while the methane conversion x or partial hydrogen pressure p_{H_2} can be used for characterization of the outlet gas composition. The latter characteristics are in the relationship following from the stoichiometric equation of reaction (8):

$$x = \frac{p_{H_2}}{2P - p_{H_2}}. \tag{11}$$

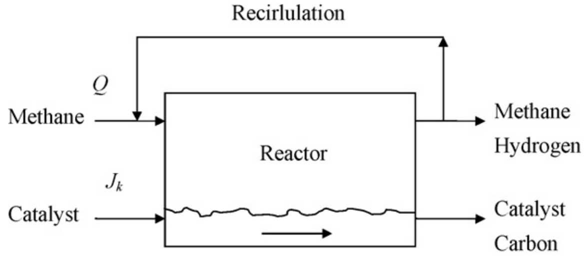

Fig. 4. Schematic of the reactor.

The partial pressure of hydrogen can be calculated from the equation of carbon balance between the gas and catalyst. In the stationary process under consideration, the carbon formed through methane decomposition is drawn away along with the catalyst from the reactor:

$$J_c x = J_k c_1, \tag{12}$$

where J_c (kg/h) is the carbon flow that enters the reactor as a constituent of methane, $J_c = 12Q/22.4$, 12 kg/kmol is the molecular mass of carbon, 22.4 m^3/kmol the volume of 1 kmol of gas at standard conditions.

It is convenient for calculations to use specific quantities such as the specific catalyst flow rate, $j_k = J_k/m_0$, and specific carbon flow rate, $j_c = J_c/m_0$, as a part of methane. When so, Eq. (12) will be rewritten in the form:

$$j_c x = j_k c_1. \tag{13}$$

While the moving catalyst is carbonized due to intensive gas recirculations at constant composition of the gas mixture, then the outlet specific carbon content, c_1, can be determined from dependence (9)

$$c_1 = c_m \operatorname{th}\left(\frac{r_m}{c_m}\tau\right), \tag{14}$$

where τ is the catalyst residence time in the reactor

$$\tau = \frac{m_0}{J_k}. \tag{15}$$

The partial pressure of methane is expressed in terms of total pressure and partial pressure of hydrogen as

$$p_{CH_4} = P - p_{H_2}. \tag{16}$$

Therefore, quantities r_m (3) and c_m (10) in Eq. (9) can be considered as functions of hydrogen partial pressure.

In view of Eqs. (11) and (14)–(16), Eq. (13) for calculating partial pressure of hydrogen will be

$$j_c x(p_{H_2}) = j_k c_m(p_{H_2}) \operatorname{th}\left(\frac{r_m(p_{H_2})}{c_m(p_{H_2}) j_k}\right). \tag{17}$$

Numerical solution of Eq. (17) gives p_{H_2}, methane conversion is calculated by Eq. (11) and outlet carbon content from the dependence following from Eq. (13):

$$c_1 = \frac{j_c}{j_k} x. \tag{18}$$

4. Calculated results and discussion

In the calculations, $T = 823$ K, $P = 1$ bar, specific methane flow rate $q = Q/m_0 = 120$ m^3/h kg, and specific catalyst flow rate j_k varies from 0.02 to 0.1 l/h.

Calculated results on dependencies of the outlet specific carbon content, c_1, on the catalyst, methane conversion, x, and partial pressure of hydrogen in the reactor, p_{H_2}, on specific catalyst flow rate j_k are illustrated in Figs. 5–7, respectively. One can see in Fig. 5 that there exists some optimal catalyst flow rate at a fixed methane flow rate to provide the maximal carbon yield.

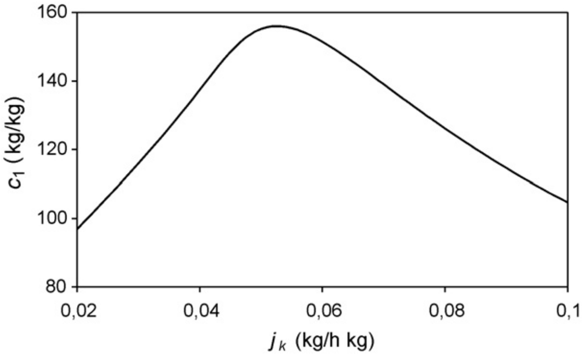

Fig. 5. Specific carbon content on the catalyst at the reactor outlet c_1 vs. j_k at $T = 823$ K, $P = 1$ bar, $q = 120$ m^3/h kg.

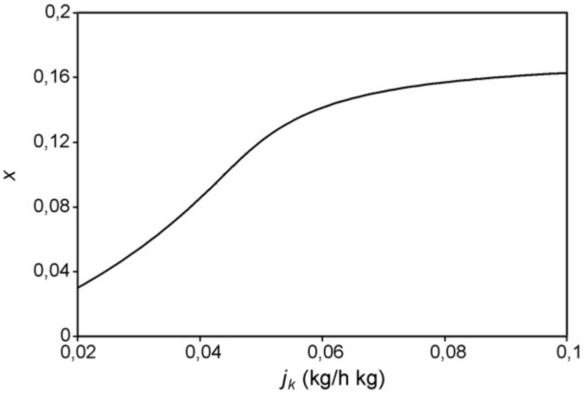

Fig. 6. Methane conversion at the reactor outlet x versus j_k at $T = 823$ K, $P = 1$ bar, $q = 120$ m^3/h kg.

The maximal specific carbon yield equal to 156 kg/kg, which is reached at the specific carbon flow rate $j_k = 0.053$ l/h, is close to the one achieved in an ideal mixing (for catalyst and gas) batch reactor at identical temperatures and specific methane flow rate (159 kg/kg) [16].

The presence of maximum in the dependence of specific carbon yield on specific catalyst flow rate at otherwise constant parameters also is characteristic of other continuous processes [19,20]. The reason is as follows. When the specific catalyst flow rate is high, the catalyst residence time is short in the reactor

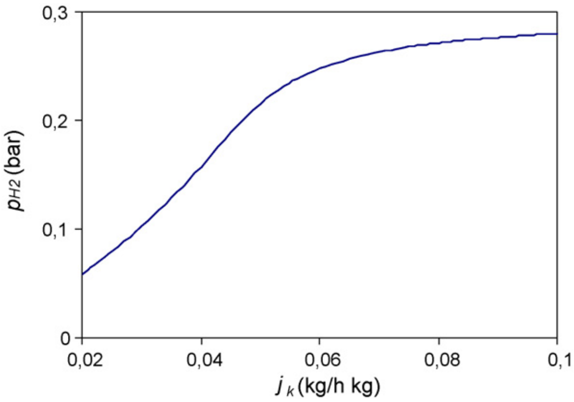

Fig. 7. Partial pressure of hydrogen in the reactor p_{H_2} vs. j_k at $T = 823$ K, $P = 1$ bar, $q = 120$ m^3/h kg.

Table 1
Comparison of continuous processes with regard to the maximal specific carbon yield at $T = 823$ K, $P = 1$ bar, $q = 120\,\mathrm{m^3/h\,kg}$

Process	Maximal specific carbon yield (kg/kg)	Specific flow rate of catalyst (kg/h kg)	Partial pressure of hydrogen in the reactor (bar)
Ideal mixing of gas and catalyst, selective material withdrawal [19]	156	0.053	0.228
Ideal displacement of gas and catalyst, counterflow [20]	107	0.13	0–0.356
Ideal displacement of gas and catalyst, straight flow [20]	128	0.074	0–0.257
Intensive gas recirculation (ideal gas mixing) and ideal catalyst displacement (the process under consideration)	156	0.053	0.228

that does not allow the carbon loading to increase considerably on the catalyst. If so, the catalyst remains in active state when escapes the reactor. The low specific catalyst flow rate results in a high Q/J_k ratio and a low methane conversion, while the carbon is practically formed in a pure methane atmosphere, i.e. under conditions favoring the highest rate of the catalyst deactivation [27]. The catalyst is fully deactivated but the carbon content appears not high (ca. 50 kg/kg).

In considering the problem of choosing the optimal reactor type, it is reasonable to compare different reactor types with regard to the maximal specific carbon yield they provide. The Table 1 gives comparative data on maximal specific carbon yield at identical conditions ($T = 823$ K, $P = 1$ bar, $q = 120\,\mathrm{m^3/h\,kg}$) in continuous processes using various type reactors and data on the specific flow rate of catalyst and partial pressure of hydrogen in the reactor for conditions with maximal specific carbon yield.

The given data show that the process under consideration and the process described in [19] provide the highest carbon yield. At the same time, the latter process is more complex in implementation; it needs additional facilities to draw the deactivated catalyst particles away from the reactor. Thus, the proposed process is preferable against the processes discussed elsewhere [19,20].

To approach the regime of ideal gas mixing, we suggested the use of recirculated gas flow. Among the other methods to provide the constant reaction mixture composition in the reactor, there may be, e.g. forced mixing of the gas in the reaction zone of the reactor.

5. Conclusions

The continuous process for synthesis of nanofibrous carbon from methane in a reactor with a moving bed of the Ni–Al_2O_3 catalyst (90 wt.% Ni) and intensively recirculated gas flow is considered. Dependencies for calculating outlet characteristics of the gas mixture and catalyst are suggested based on the model of a reactor with ideal gas mixing and ideal catalyst displacement. The specific catalyst flow rate providing the maximal carbon yield is determined at $T = 823$ K, $P = 1$ bar, and specific methane flow rate equal to $120\,\mathrm{m^3/h\,kg}$. Comparison of various types of continuous reactors shows that the reactor under consideration is preferable.

Acknowledgements

The work was supported by the Ministerial Scientific Program *Development of Scientific Potential of high School* (Project 60059).

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