Chemical Engineering Journal 171 (2011) 255–271

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Oxidative coupling of methane in a fluidized bed reactor: Influence of feeding policy, hydrodynamics, and reactor geometry

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ARTICLE INFO

Article history:
Received 13 August 2010
Received in revised form 22 March 2011
Accepted 23 March 2011

Keywords:
Oxidative coupling of methane
Fluidized bed reactor
Reactor design
Computatuional fluid dynamics
Fluidized bed membrane reactor

ABSTRACT

Oxidative coupling of methane (OCM) is suggested to be a promising process for the conversion of the abundant natural gas into useful chemicals. However, this reaction faces many drawbacks such as low yields for higher hydrocarbons, fast catalyst deactivation, and huge heat effects of the reaction. Only a well-designed fluidized bed reactor is able to overcome effectively those disadvantages and to provide a satisfactory continuous operation. However, design approaches for fluidized bed reactors are still based on models developed during 70s and 80s, which cannot take into account various hydrodynamic effects on the reactor performance. Thus, a reactor designer has usually to rely on extensive experiments in order to improve the classical fluidized bed reactor design.

In this work, the relevance of hydrodynamics, reactor geometry, and feeding policy on the performance of a fluidized bed reactor for the OCM is shown. For this purpose, several case studies of fluidized bed reactors are simulated in full 3D geometry under the same reaction conditions, but with different reactor geometries and feeding policy. These studies show the significance of hydrodynamic parameters for the reactor performance, and moreover, how fluidized bed reactor performance can be improved by a careful study of coupled momentum-mass transport-reaction phenomena. Furthermore, it can be demonstrated that a suitable distributed feeding policy of oxygen provides an improved yield while a traditional fluidized bed reactor design results in an inferior performance among all investigated cases.

1. Introduction

Oxidative coupling of methane (OCM) is a promising process for converting huge reserves of natural gas into liquid fuels or useful chemicals [1]. Since the pioneering work of Keller and Bhasin in 1982, there has been an intensive research on the topic of OCM [2]. These authors showed that it is possible to convert methane to ethylene in a gas phase using a metal oxide catalyst in the presence of oxygen and under temperatures between 500 and 1000 °C. This work initiated a great interest in this reaction since it represents a direct conversion route of natural gas to high valuable intermediates. Moreover, there exist a number of different reactions for natural gas conversion. A comprehensive review of potential reaction paths for conversion of natural gas is given in [3]. Although several alternatives have though been proposed so far, none of them have yet found an industrial application.

Currently, methane is used almost exclusively for power generation and heating as well as in a smaller amount for syn-gas production via partial oxidation or steam reforming. The latter application is the only industrially implemented methane conversion process, where methane is used as a raw material [4]. However, there are numerous drawbacks of such process, e.g. CO_2 selectivity in case of partial oxidation, or endothermicity in case of steam reforming. Furthermore, if liquid fuels or fine chemicals are to be produced, another catalytic process is required [4,5]. Hence, oxidative coupling of methane as a one-step conversion process provides a reasonable alternative for methane to syngas conversion processes. Furthermore, if high ethylene yield can be achieved, oxidative coupling of methane will become the key technology for both chemical and petrochemical industry.

However, oxidative coupling of methane faces several drawbacks, out of which selectivity towards ethylene is the critical one. So far only a selectivity of up to 70% have been achieved with more than 30% methane conversion, and therefore, yield of ethane and ethylene has been limited so far to less than 25% in conventional reactors [1,6,7]. It has been shown previously that low oxygen levels limit the conversion of methane, but are able to provide high selectivity by controlling the subsequent product combustion. On another hand, if high yield and conversion are required there is a need for more oxygen in the feed, and thus selectivity drops significantly because of the product combustion. Another difficulty for the practical application is the huge heat released during the reac-

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doi:10.1016/j.cej.2011.03.077

Nomenclature

$\beta_{g,s}$	interphase exchange coefficient
C_D	drag coefficient
d_s	solids diameter
e_{ss}	restitution coefficient
$E_{a,j}$	energy of activation for the *j*th reaction
ε_g	solids volume fraction
ε_s	gas volume fraction
f	gas solid friction coefficient
φ	angle of friction
g	gravitational acceleration
$g_{0,ss}$	radial distribution function
ΔH_{ads}	heat of adsorption
h_i	molar enthalpy for the *i*th phase
$J_{i,j}$	diffusive mass flux
K_j	adsorption constant for *j*th component
$k_{0,j}$	predexponential factor for *j*th reaction
λ_s	solids bulk viscosity
m	reaction order for 1st reactant
M_j	molecular mass for *j*th component
μ_s	total solids viscosity
$\mu_{s,col}$	colisional viscosity part
$\mu_{s,kin}$	kinetic viscosity part
$\mu_{s,fr}$	frictional viscosity part
μ_g	gas viscosity
n	reaction order for 2nd reactant
$\nu_{j,k}$	stoichiometry matrix
P	pressure
P_s	solids pressure
π	pi number, 3.14
$\bar{q}_i$	diffusive heat flux
$Q_{i,j}$	heat exchange rate between phases *i* and *j*
r_k	reaction rate for the *k*th reaction
Re_s	Reynolds number
ρ_g	gas density
ρ_s	solids density
$S_{i,j}$	mass source term for *j*th species
$\bar{\bar{\tau}}_g$	gas stress tensor
$\bar{\bar{\tau}}_s$	solids stress tensor
τ_s	particular relaxation time
Θ_s	granular temperature
$v_{r,s}$	solids terminal velocity
$\vec{w}_g$	gas velocity vector
$\vec{w}_s$	solids velocity vector
$Y_{i,j}$	mass fraction of *i*th species in *j*th phase

tion, which is a consequence of fast reactions and very high heat effects [1,8]. Thus, severe hot spot formation has been observed in packed bed reactors even for small diameters [9]. From a practical point of view, the first mentioned drawback can be overcome with the use of a better catalyst and improved reaction engineering. However, the second drawback related to the enormous heat effect can only be solved by an enhanced reactor design since it is also influenced by thermodynamics and fluid dynamics, not only by reaction kinetics.

In the past 25 years, huge efforts have been put in catalyst development for the OCM process. The results reviewed by [1,6,7] show that yields of less than 25% still represent the maximum one can expect from a conventional OCM reactor. From these reviews it seems that the catalyst development does not allow further yield increase because of interplay between heterogeneous and gas phase reactions. Thus, oxidation of both methane and higher reaction products seems to be unavoidable in the case of higher oxygen content in the feed. Therefore a controlled oxygen feeding has been initially proved to be successful by [10] using a membrane reactor (MR). After this, numerous research on membrane reactors have been done on OCM in both theory and practice [11–21].

The use of membrane reactors is still under development. Idea behind a membrane reactor is to allow very small oxygen amount to pass continuously in to the reaction zone in order to activate methane and allow a radical chain reaction to proceed, while limiting the undesired combustion reactions. This can be done in different ways by using a porous membrane, dense membrane, catalytic membrane or perovskyte membrane. It has theoretically been proved that they can provide well over 30% yield [11,12]. Nevertheless, only 28% yield has been reported in porous MR [13] and around 35% in a catalytic MR [20]. The highest yield reported ever for one OCM reactor is over 50% with the use of a CSMBR (chromatographic simulated moving bed reactor) [22]. However, such reactor concept has still to be developed in detail before any large scale application.

The fluidized bed reactor has been designated by different authors as the best reactor concept for OCM [1,8]. This is mainly because of the huge reaction heat, which cannot be managed by any packed bed reactor. Moreover, the ability to operate isothermally and to avoid a temperature runaway and at the same time to continuously re-circulate or even to change deactivated catalyst makes the fluidized bed a very attractive reactor concept for the OCM reaction. There have been a number of investigations in the 90s around the fluidized bed reactor concept [23–31]. All of these studies showed that only a yield of less than 19.4% was accessible in a fluidized bed reactor, and thus, limiting its yield to the similar restriction as in the case of a fixed bed reactor.

The concept of a fluidized bed membrane reactor has already been proposed for different applications such as for the reforming of hydrocarbons, where its implementation aims at removing hydrogen from the reactor while enabling the reaction equilibrium shift towards the desired products. Moreover, several applications of oxidative dehydrogenations similar to OCM have been proposed as well. So for instance, Deshmukh et al. [32,33] showed that an externally fluidized bed membrane reactor can improve the performance of oxidative dehydrogenation of propane and butane to maleic anhydride. On the other hand, the works in [34–36] showed that a fluidized bed membrane reactor improves the yield of partial oxidation of methanol to formaldehyde in comparison to conventional reactors. An increased performance of the oxidative hydrogenation of ethane in a fluidized bed membrane reactor in comparison to fixed, fluidized, and membrane reactors was reported in [37]. In addition, a detailed review of potentials and problems arising with the application of fluidized bed membrane reactors was given by Deshmukh et al. [38], in which the application of fluidized bed membrane reactors was highlighted for the family of partial oxidation reactions. However, no investigation of fluidized bed membrane reactor for the OCM reaction has been reported at all. In this work, we conduct a model based investigation of the fluidized bed membrane reactor performance while comparing it with different configurations of the fluidized bed reactor.

Fluidized bed reactor design and scale-up has been an issue for more than 50 years [39–42]. Industrial application of OCM reactors has only been discussed briefly in some published works [1,8,43]. Several cases of poor scale-up of fluidized bed reactors for different application has been reported in book of Kunni and Levenspiel [40], and the root of these failures was basically poor knowledge of fluidized bed hydrodynamics. Since 40s, when fluidized bed technology literally exploded, numerous correlations were published for the prediction of several bed parameters such as bubble diameter, minimum fluidization velocity, bubble rise velocity, bubble coalescence, breakup, and similar. Using those parameters and the two-phase theory of fluidization, several models like bubbling bed