Fuel 107 (2013) 254–260

Contents lists available at SciVerse ScienceDirect

Fuel

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

Modeling of fixed bed methanation reactor for syngas production: Operating window and performance characteristics

Naren Rajan Parlikkad [a,1], Stéphane Chambrey [a], Pascal Fongarland [a,d,*], Nouria Fatah [b], Andrei Khodakov [a], Sandra Capela [c], Olivier Guerrini [c]

[a] Unité de Catalyse et de Chimie du Solide (UCCS), UMR CNRS 8181, Ecole Centrale de Lille, Cite Scientifique, BP 42, 59651 Villeneuve d'Ascq Cedex, France
[b] Unité de Catalyse et de Chimie du Solide (UCCS), UMR CNRS 8181, Ecole Nationale Supérieure de Chimie de Lille, Ecole Centrale de Lille, Cite Scientifique, BP 42, 59651 Villeneuve d'Ascq Cedex, France
[c] GDF-Suez, Direction de la Recherche, 361, avenue du Président Wilson, BP 33, 93211 Saint-Denis La Plaine Cedex, France
[d] Université Lyon 1, UMR CNRS 5256, IRCELYON, Institut de recherches sur la catalyse et l'environnement de Lyon, 2 avenue Albert Einstein, F-69626 Villeurbanne, France

HIGHLIGHTS

- Developed phenomenological reactor engineering model for methanation.
- Pseudo-homogeneous and heterogeneous reactor models were developed.
- Simulated fixed bed methanator to study the effect of inlet feed conditions.
- Water present in feed results in decrease in catalyst inventory.
- Pore diffusion plays important role in computing actual catalyst inventory.

ARTICLE INFO

Article history:
Received 11 June 2012
Received in revised form 9 January 2013
Accepted 10 January 2013
Available online 31 January 2013

Keywords:
Substitute natural gas
Methanation
Fixed bed reactor
1D pseudo-homogeneous model
1D heterogeneous model

ABSTRACT

The present work focuses on the development of phenomenological model for the bio-syngas to methane conversion process. One dimensional heterogeneous and pseudo-homogeneous model were simulated for a typical pilot plant scale fixed bed methanator processing 55 mol/h of CO (total molar flow rate of 310 mol/h) with inlet composition of $H_2/CO = 3$, $CO_2/CO = 1$, $CH_4/CO = 0.5$ at 550 K and 1 atm. Performance of the fixed bed reactor at different operating conditions like CO_2/CO ratio, H_2/CO ratio, effect of H_2O in the feed was studied. It was found that for feeds that were not pre-enriched with hydrogen, presence of water and water gas shift activity was found to decrease the catalyst inventory substantially. CO_2 in the inlet feed stream would help to decrease the temperature due to dilution effect and more importantly, can be chosen to maximize methane yield per mole of CO converted. Further, the model was simulated to predict the performance characteristics of reactor with a mixture containing two types of catalyst, one of them being specifically added to increase H_2/CO ratio in feed through water gas shift reaction. The work also laid the importance of incorporating pore diffusion and external mass transfer locally in the computation of actual catalyst inventory and reactor volume. The work was useful in selection of operating window and assessing the various viable options for an industrial reactor. The model developed will serve in selection of operability window for commercialization of substitute natural gas synthesis (SNG) process.

1. Introduction

The development of novel technologies for production of alternative fuels has gained high interest in recent years, owing to the frequent fluctuations seen in the price of fossil fuels and concerns about their uninterrupted supply. One possibility to make of use of biomass is to convert biomass via a thermo-chemical process into valuable hydrocarbons. Syngas produced from biomass gasification can further be converted into higher hydrocarbons through the Fischer–Tropsch route, or to methane via the methanation route to produce substitute natural gas (SNG). The main interest to produce bio-SNG is the possibility to use the existing natural gas grid distribution network to distribute the gas for domestic heating purposes. More so, bio-SNG research is of specific interest in European countries [1–3], which meets a large part of its natural gas

* Corresponding author.
E-mail address: pascal.fongarland@ircelyon.univ-lyon1.fr (P. Fongarland).
[1] Present address: School of Chemical and Biotechnology, SASTRA University, Thanjavur 613 401, Tamilnadu, India.

0016-2361/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.fuel.2013.01.024

Nomenclature

E	activation energy for the chemical reaction, J/mol
k	intrinsic reaction rate constant, (units as given in Table 1)
k^0	pre exponential factor for the intrinsic rate constant, (unit as given in Table 1)
K_i	adsorption coefficient for the component i, bar
K_i^0	pre exponential factor for the adsorption rate coefficient of component i, bar
K_j	equilibrium constant for the reaction j, (in appropriate units according to reaction)
p	partial pressure, Pa
P	pressure, Pa
r_i	rate of reaction of component i per unit volume of reactor, mol/m^3 s
r_i''	rate of reaction of component i per unit mass of catalyst, mol/kg$_{cat}$ s
R	universal gas constant, J/mol K
T	temperature, K
u_g	superficial gas velocity, m/s
X	percentage conversion, dimensionless
y_i	mole fraction of the component i, dimensionless
Y	percentage yield, dimensionless
z	axial position, m

Greek letters

ΔH_i	heat of adsorption of component i, J/mol
η	effectiveness factor to account for pore diffusion with reaction, dimensionless
η_{global}	global effectiveness factor including external mass transfer, dimensionless

Subscripts

A, B, ...	component index
a, b, ...	stoichiometric coefficients
i	component index (CO, CO_2, CH_4, H_2, H_2O)
j	reaction index (methane reforming, WGS)
s	solid phase or catalyst particle

Abbreviations

1D	one dimensional
2D	two dimensional
FBR	fixed bed reactor
SNG	substitute or synthetic natural gas
WGS	water gas shift reaction
rWGS	reverse water gas shift reaction

requirement through imports. Despite the fact that methanation reaction is known since several decades, very few studies have focused on the production of SNG from syngas obtained from biomass and on the development of robust engineering model to simulate the methanation reactor. The processes developed in the past were mainly concerned with the coal gasification to methane and are very different from biomass gasifier units where the plant are smaller due to the lower amount of the feedstock. This is why a better optimization is required for bio-SNG production unit.

CO methanation is a highly exothermic and a reversible reaction, specifically at higher temperatures. The reaction is typically catalyzed by transition metals like Nickel and Ruthenium, with Nickel being most favored catalyst industrially because its lower cost [4]. CO methanation is often accompanied by water gas shift (WGS) and carbon deposition. Elucidation of CO kinetics is difficult owing to the occurrence of these simultaneous reactions and the high activity reported on Nickel catalysts leading to possible mass/heat transfer control even at the laboratory scale. The number of kinetic studies and mechanisms reported in open literature are testimony for the same [4–8]. The industrial process design and development of methanator is complex in nature owing to the issues of exothermicity, mass transfer, equilibrium limitation, occurrence of secondary reactions like water gas shift and the effect of feed composition. For instance, Kopyscinski [4] through experiments and simulation studies on fluidized bed methanation reactor showed that capturing the characteristic features of fast exothermic methanation reaction was rather difficult and hence remains a challenge. They observed that most of the reaction was completed within few mm from inlet (roughly in about 10 mm) and was accompanied by steep increase in reactor temperature.

In this background, the prime focus of the present work was set to develop a simple yet robust lower order phenomenological reactor engineering model for the methanator that would essentially capture the fundamental operations of the methanation process and help to provide guidelines for the industrial operation of methanator. The objective of the work was to study the performance aspects and key features of a fixed bed methanator and subsequently be able to synergize the model outputs with the biomass to SNG process.

2. Mathematical model

In the present work, fixed bed reactor (FBR) for the methanation process was modeled following one dimensional approach. The one dimensional model ignores the presence of radial gradients in the bed. However a-priori calculations do not exclude significant external mass transfer, interparticle heat transfer limitation in the fixed bed methanation reactor. For instance, the observed Mear's criterion [9,10] for interphase mass transfer (external mass transfer criteria) was found to be greater than 1 (hence not satisfied) for a typical 2.5 mm fixed bed catalyst at 550 K. Similarly the interparticle heat transfer criterion was also found to be not satisfied at the typical operating conditions (Table 2). Nonetheless, given the mandate to develop reactor engineering model with an industrial perspective and the laboratory constraints to measure and obtain reliable local concentration, temperature data (2D data); it was thought judicious to proceed initially with one dimensional approach and improvise the same in later stages of the project cycle. Both 1D pseudo-homogeneous and 1D heterogeneous framework were adopted to simulate the performance of the FBR. In the heterogeneous model, the effectiveness factor for the catalyst was computed locally along the reactor and coupled with the mass and energy balance equation for the gas phase. In contrast, in the pseudo-homogenous model, the effectiveness factor was assumed at a fixed value (a user input) and was invariant within the model simulation. The pressure drop in the reactor was obtained from Ergun relation [11]. Detailed description of the 1D heterogeneous and 1D pseudo-homogeneous model can be found from Froment and Bischoff [12] and is not presented here for sake of brevity. The final conservation equations are provided in the Supplementary material.

2.1. Methanation kinetics

In this work, the kinetic expression used for the CO methanation was based on Xu and Froment [6]. Experiments were conducted in a laboratory catalytic test facility equipped with a micro-Berty reactor (Autoclave Engineers) and using a proprietary