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Membrane reactor system model for gas conversion to benzene

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ABSTRACT

In the direct nonoxidative conversion of methane gas to liquid chemicals, it has been shown that continuous removal of produced hydrogen is a way to overcome the thermodynamic limit of low equilibrium methane conversion. A plug-flow, isothermal membrane reactor model was developed for the conversion of methane gas to aromatics over Mo/H-ZSM5 and integrated in an Aspen Plus process model using COCO (CAPE-OPEN to CAPE-OPEN) Simulator. Parameters such as reaction rate constants and equilibrium coefficients required by the model were obtained using experimental data. The reactor employs a simplified reaction network whose product distributions agree well with other models and published results. Damkohler number of 0.5 and a dimensionless hydrogen removal parameter δ of 10 were found to be the optimum parameters for benzene selectivity. The reactor model being embedded in the process allows for more detailed exploration of the impact of reactor parameters on the process as a whole. Methane conversion remains at 10.9% and 20% for each case with or without recycle. Benzene molar flow increases by 72% for the single pass configuration when $Da = 0.5$ and $\delta = 10$ are used; however, naphthalene molar flow increases by 215%.

1. Introduction

Our rapidly growing population imposes a large demand on products of the organic chemical industry, the manufacture of which heavily relies almost entirely on petrochemicals. Additionally, developing technologies in unconventional oil recovery are producing great amounts of oil and gas from previously inaccessible rock formations [1]. The U.S. Energy Information Administration reports that gross natural gas withdrawal for January 2015 was 2840 Bcf. Meanwhile, storage increased from 825 Bcf in April 2014 to 1476 Bcf in April 2015 [2]. With the depletion of conventional petroleum reserves and the abundance of natural gas, methane is slated to become the most important hydrocarbon feedstock for synthesizing fuels and chemicals.

Benzene is an important petrochemical precursor to chemicals such as ethylbenzene, cumene, and cyclohexane. These are further processed make dye, detergent, adhesives, textiles, rubber, plastics, and more. The prevalence of benzene in such a wide variety of industries is such that worldwide benzene demand is often used as an economic bell-weather. Recent reports have demonstrated an increasing demand for benzene spurred by industrial development in the Eastern hemisphere, the demand is projected to grow at a rate of 3% per year reaching 50 million metric tons by 2018 [3].

1.1. Current benzene production methods

Most (~95%) of the world benzene supply is currently petroleum derived using one of three main methods: catalytic reforming, toluene hydrodealkylation, and from steam cracking of naphthas to produce pyrolytic gasoline [4].

Catalytic reforming produces approximately 30% of the world benzene supply [5]. Aromatic molecules are produced from dehydrogenation of cycloparaffins, dehydroisomerization of alkyl cyclopentanes, and cyclization and subsequent dehydrogenation of paraffins [5]. Toluene hydrodealkylation contributes 25–30% of the world benzene supply. Toluene is mixed with a hydrogen stream and passed through a catalytic reactor using chromium or molybdenum oxide [6]. The remaining benzene produced via the pyrolytic gasoline route constitutes steam cracking of heavy naphthas or light hydrocarbons, such as propane or butane, are used to make ethylene. The by-product of this process is a drip oil typically composed of 65% aromatics, which contain approximately 50% benzene [7].

1.2. State-of-the-art in natural gas conversion

Much work has been done in the search for economical ways to convert natural gas methane directly to chemicals. Presently, methane is converted to intermediates such as syngas or methanol and subsequently reacted to form a wide variety products [8]. The

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Nomenclature

C_i	concentration of species *i*
Da	Damkohler number
d	reactor diameter, m
f_j	dimensionless rate expression for reaction *j*
F_i	molar flow of species *i*, mol/s
K	equilibrium constant, mol m^{-3}
$J_{CH_4,o}$	methane inlet flux, mol s^{-1} m^{-2}
J_{H_2}	hydrogen flux, mol s^{-1} m^{-2}
L	reactor length, m
l	membrane thickness, m
$m_{c,i}$	mass of carbon in species *i*
n_i	number of carbon atoms in species *i*
P_{H_2}	hydrogen permeability, mol m^{-1} Pa^{-1} s^{-1}
p	pressure, Pa
S_i	selectivity of species *i*
X_{CH_4}	methane conversion

Greek letters

α_j	permeability ratio in reaction *j*
β_i	reaction rate constant ratio, $\frac{k_i}{k_1}$
ϕ_i	dimensionless flow rate of species *i* in reaction side
λ_{ij}	stoichiometric coefficient for species *i* in reaction *j*
δ	ratio of permeation rate to reaction rate
ξ	dimensionless axial distance
y_{it}	mole fraction of species *i* on tube side
y_{is}	mole fraction of species *i* on shell side

non-syngas routes include oxidative and non-oxidative processes. Oxidative conversion is a coupling process to produce olefins, which can be further converted to liquid hydrocarbons. The oxidative processes are highly exothermic and potentially hazardous. Additionally, these processes require pure oxygen and result in limited selectivity to desired products. In summary, the syngas (indirect) and oxidative coupling (direct) routes have numerous challenges. The direct conversion of methane to aromatics through non-oxidative pathways is an attractive alternative to the above mentioned methods.

Dehydroaromatization (DHA) of methane is one such direct conversion reaction producing aromatic hydrocarbons as well as hydrogen. Molybdenum promoted H-ZSM5 catalysts have been shown to adequately activate the strong C–H bonds in methane and aromatize the resulting CH_x species leading to the formation of various aromatics with ~90% selectivity [9]. The large quantity of hydrogen byproduct is responsible for thermodynamic limitations resulting in low (~12%) equilibrium methane conversion at 973 K [10]; therefore, a hydrogen removal method must be implemented to achieve industrially acceptable benzene yields [8,11].

Recent modeling efforts have focused on the kinetic aspects of the problem such as activation of methane [8] and the effect of various parameters on hydrocarbon yield and selectivity [12,13]. Prior modeling efforts constituted a semi-empirical kinetics model and assessing the impact of a hypothetical membrane separator. There is a significant need to develop a semi-empirical model that represents a reactor–membrane assembly and integrate the model with process simulation. Using this integrated model, an analysis of the effect of key parameters on the production process at large may be conducted to more confidently determine feasibility of the technology for industrial use and optimum operating conditions.

The overall modeling methodology is described in Fig. 1.

2. Reactor model

A membrane reactor model was created in Matlab R2013b and interfaced with Aspen Plus v8.8 as a CAPE-OPEN User Model. The reactor scheme in Matlab consists of isothermal 1D differential plug flow reactor equations describing a simplified set of three equilibrium reactions which have been shown to adequately describe catalytic methane conversion to aromatics [14].

A dimensionless mole balance equation (Eq. (1)) including Fickian hydrogen transport through a membrane much thinner than the reactor diameter has been developed by Li et al. and here is used on the reaction side [11].

$$\frac{1}{Da}\frac{d\phi_i}{d\xi} = \sum_{j=1}^{n}\lambda_{ij}\beta_j f_j(K,p) - \delta\alpha_i(y_{it} - y_{is}) \tag{1}$$

Inputs to the model are the feed composition and flow rate, as well as Damkohler number and δ, which are qualitatively defined as the ratio of reactant conversion rate to reactant inlet rate, and the ratio of permeation rate to reaction rate, respectively [11].

$$Da = \frac{Lk_1}{J_{CH_4,o}} \tag{2}$$

$$\delta = \frac{4P_{H_2}p}{dlk_1} \tag{3}$$

With both of these parameters, key variables such as reactor and membrane dimensions, and reaction conditions are taken into account.

Experiments using 3% Mo/H-ZSM5 were carried out under the conditions in Table 1. Equilibrium constants for the reactions in Table 2 were calculated using the van't Hoff equation and confirmed using a Gibbs minimization reactor in Aspen Plus. Aspen will calculate phase and chemical equilibrium such that Gibbs

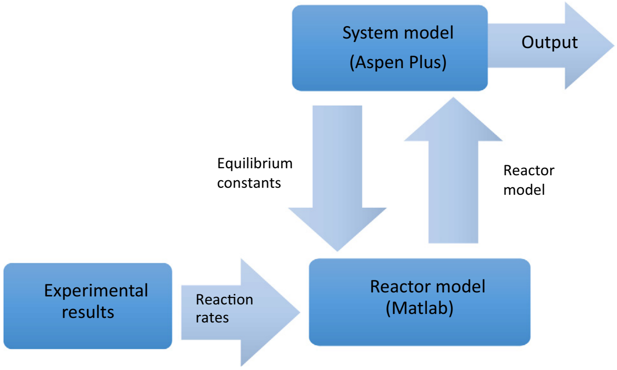

Fig. 1. Overall modeling methodology.

Table 1
Reaction and catalyst specifications.

Mo/H-ZSM5 (Mo/Al = 0.26) Amount of catalyst: 1 g Particle size: 180–250 μm Reactor ID: 8 mm Space velocity: 1500 cc/g_{cat}/h	Mo/H-ZSM5 (Mo/Al = 0.43) Amount of catalyst: 0.25 g Particle size: 180–250 μm Reactor ID: 8 mm Space velocity: 3500 cc/g_{cat}/h
Activation was done in helium (100 sccm) for 2 h at 973 K	Activation was done in helium (50 sccm) for 2 h at 973 K
Feed: 85% CH_4/Ar at 23.6 sccm (CH_4 21.24 sccm) Temperature (T_{set}): 973 K Average pressure: 1.25 bar All lines heated up to $T > 453$ K	Feed: 85% CH_4/Ar at 13.9 sccm (CH_4 12.5 sccm) Temperature (T_{set}): 973 K Average pressure: 1.0 bar All lines heated up to $T > 453$ K