A novel polygeneration process to co-produce ethylene and electricity from shale gas with zero CO_2 emissions via methane oxidative coupling

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ABSTRACT

A techno-economic analysis of a novel process to co-produce ethylene and electricity using a recently developed methane oxidative coupling catalyst is presented. Several design variants are considered, featuring the use of traditional gas turbines, chemical looping combustion, and 100% carbon dioxide capture. Mass and energy balance simulations were carried out using Aspen Plus simulations, and particle swarm optimization was used to determine the optimal process design under a variety of market scenarios. A custom model for the gas turbine section was used to ensure that the negative impacts of various cooling strategies were factored into the analysis. The results show that by synergistically co-producing power and ethylene using this catalyst, ethylene can be produced at costs close to traditional steam cracking methods with nearly zero carbon dioxide emissions, even when factoring in the relatively poor conversion and selectivity of the chosen catalyst.

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1. Introduction

Olefins such as ethylene and propylene are among the most important feedstocks of petrochemical plants [1] since they are fundamental materials for many applications in the polymers and plastics industries. Globally, annual ethylene production was about 143.4 million tonne of ethylene in January 2013 [2], and it has been predicted that the worldwide demand for olefins such as ethylene will grow steadily by around 1.5–4.1% per year [2,3] regardless of the crude oil price. Traditionally, olefins are produced through different types of steam cracking processes depending on the industry. For example, in the oil industry naphtha is produced from petroleum, which can then be converted to olefins via a naphtha cracking process, while in the natural gas industry, ethane is recovered from natural gas and then converted to olefins via the ethane cracking process. In either type of steam cracker, the feedstock (naphtha or ethane) is "cracked" by reacting it with high pressure steam in a series of endothermic reactions at 600–900 °C [1].

However, recent shifts in environmental attitudes and energy markets have brought to light some new challenges and some new opportunities for the olefins industry. First, these processes rely heavily on the combustion of fossil fuels to supply the heat requirement in the cracking furnace of olefin plants which is extremely energy intensive and results in as many 200 million tons of CO_2 emitted per year worldwide [4]. The life cycle analysis results show that the greenhouse gas emissions of the typical oil to olefin plants is more than 4 tonne $CO_{2,eq.}$ per tonne olefins [5]. This is a significant amount of emissions which, if prevented, would be equivalent to taking about 42 million passenger cars off the road [6]. Unfortunately, there has been very little effort to reduce the CO_2 emissions from this process.

Second, from a North American economic perspective, the primary raw material for ethylene production (crude oil) is becoming increasingly difficult to use. Though North American markets continue to have access to plentiful oil, the reserves of lighter crudes suitable for naphtha production (and therefore for ethylene production) are depleting. Heavier crudes may be used instead, but these are more expensive to convert into the light products for ethylene production. A more attractive alternative is natural gas, which due to the shale gas boom beginning in 2009 experienced a major decline in price compared to oil [7] and coal [8]. In fact, oil currently costs more than 3 times as much per joule of energy than natural gas [9].

Therefore, because of the low price of natural gas and shale gas it makes economic sense to use a different route to convert the plentiful methane contained in the gas into olefins. Two processes using methane are possible, namely methanol-to-olefins (MTO) and oxidative coupling of methane (OCM). In the MTO process, feeds like natural gas [10–12], coal [13] or biomass [14] are firstly converted to synthesis gas, which is then converted to methanol

Nomenclature

ASU	air separation unit	NPV	net present value
CLC	chemical looping combustion	OCM	oxidative coupling of methane
DGA	diglycolamine	PSO	particle swarm optimization
DME	dimethyl ether	R-50	methane refrigerant
$E_{Ethylene}$	yield of ethylene production over ethane	R-1150	ethylene refrigerant
Eth.	ethylene (price)	R-1270	propylene refrigerant
Eth. base	ethylene (price), base case	SG	shale gas (price)
F_i	molar flow rate of component i	SGB	shale gas (price), base case
GA	genetic algorithm	S_i	selectivity of component i
GCT	gas combustion turbine	X_i	% conversion of component i
HHV	higher heating value		
HRSG	heat recovery steam generator		

and then dimethyl ether (DME). Then, olefin gases are produced through DME conversion to ethylene, propylene, butene and pentene along with carbon dioxide, H_2O and saturated hydrocarbons (ethane, propane and butane), in the presence of catalyst. The MTO process was developed at Mobil Oil in 1977 [15] and is offered for commercialization by several companies such as UOP, ExxonMobil [4] and Total [11]. Selectivity and product distribution of MTO over different catalysts such as SAPO-34 [16–20], KCl–LnCl$_3$ [21] and ZSM-5 [22,23] are an area of active development.

The OCM process has been studied and developed since 1980 [24] based on catalytic oxidative dimerization of methane to convert methane directly to ethylene [4] and ethane (by-product) [24–26]. In this method, methyl radicals are formed as a product of methane partial oxidization. After ethane formation from these methyl radicals, it is dehydrogenated into ethylene. The gas conversion, which can be adjusted by changing the relative amount of oxygen used, affects the selectivity of desired components in the product stream. Various reaction kinetics, reactor design, and operating conditions are described by Keller and Bhasin [24], Sinev et al. [27], Mleczko and Baerns [28], and Zaman [29]. Huff et al. [30] designed a pilot plant based on British Petroleum patent [26], and other catalysts. Taken together, their results indicate that poor methane conversion and product selectivity are a major drawback of this process due to the relatively stable properties of methane itself [24].
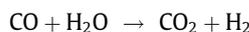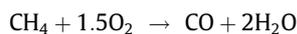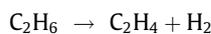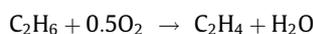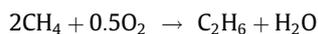
However, recent developments of newer and more effective catalysts have made the OCM process attractive again. For example, a La$_2$O$_3$/CaO catalyst has exhibited significant promise for converting gas to olefins with relatively high activity and selectivity compared to other catalysts [31,32]. This catalyst shows promise both as use in a traditional packed bed reactor design, as well as a membrane reactor design [33,34]. However, to the best of our knowledge, there have been no processes proposed at the industrial scale using this catalyst for high-methane shale gas feeds. In addition, there have been no processes of this type designed for near-zero CO_2 emissions.

Therefore, we present in this work the first process using this OCM catalyst for high-methane shale gas and feature an optional 100% CO_2 capture system. In this process electricity, ethane and in some scenarios propane are produced as important co-products, classifying it as a "polygeneration" process. Two different electricity production technologies are considered, namely gas combustion turbines (a traditional approach) and chemical looping combustion (an advanced approach). Aspen Plus simulations, custom models (for certain key unit operations), and derivative-free optimization techniques were used to create a collection of suitable design possibilities, each of which might be chosen depending on different business priorities, market conditions, or regulatory scenarios. A net present value approach was used to determine

the economic feasibility of the proposed designs, and a sensitivity analysis was used to explore the effect of uncertainties in market conditions.

2. Process description

The simplified schematic of this process is shown in Fig. 1. It consists mainly of six sub-sections: direct ethylene synthesis from shale gas using an OCM reactor, compression, CO_2 removal, product recovery (a demethanizer and C$_2$ splitter), power generation, and CO_2 compression (optional). The OCM reactor is a gaseous fluidized bed reactor that uses a La$_2$O$_3$ (27 wt.%)/CaO (73 wt.%) catalyst at about 800 °C. The contact time (mass of catalyst divided by volumetric gas flow rate) should be also less than 250 kg s/m³) [32]. The operating conditions and outlet composition of the reactor is based on a model derived from the experimental work of Godini et al. [35] and described in Section 3.3. The main OCM reactions and side reactions over the La$_2$O$_3$/CaO catalyst at 750–900 °C are as follows, noting that the primary products are ethane (C$_2$H$_6$) and ethylene (C$_2$H$_4$) [35,36]:

$$2CH_4 + 0.5O_2 \rightarrow C_2H_6 + H_2O$$

$$C_2H_6 + 0.5O_2 \rightarrow C_2H_4 + H_2O$$

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

$$CH_4 + 1.5O_2 \rightarrow CO + 2H_2O$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

The most important property that affects the selectivity and conversion in the reactor is the ratio of inlet methane to oxygen. Raising the CH_4/O_2 ratio increases the catalyst selectivity in favor of ethylene production but reduces the conversion rate. Therefore, this ratio should be determined such that the maximum NPV can be achieved (see Section 4.1 for more detail).

Then, the product stream is compressed and sent to the amine unit (diglycolamine) to remove CO_2. After CO_2 removal, the ethylene and ethane products are separated from unreacted gases by using two separation columns with condenser temperatures so cold such that a refrigeration cycle is required to provide cooling (Fig. 2).

The unreacted gas can be either recycled to the OCM reactor (as in the traditional version of this process) [29,37], used as fuel for power generation, or a mix of both. Many options for power generation are available. A classic gas combustion turbine can be used, in which the fuel is combusted in air to spin a turbine and produce