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Evaluation of the process of oxidative coupling of methane using liquefied natural gas from deposits of Krasnoyarsk region

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Abstract

A flow sheet diagram for the process of converting of LNG of Krasnoyarsk region is considered. Process comprises reactors for oxidative methane coupling (OCM) and ethane dehydrogenation utilising heat of OCM reaction, products and reagent recycling and block of product separation, which operates at cryogenic temperature and atmospheric pressure. Mass and heat balances for different cases were calculated. It is shown that utilisation of LNG as a cooling agent has a beneficial effect on power consumption. Simulation shows that substantial increase of yield of ethylene (up to 50%) can be achieved even with a moderate performance catalyst of OCM. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: LNG; OCM; Ethylene production

1. Introduction

Northern areas of Krasnoyarsk region have large stocks of natural gas. Distinctive peculiarity of natural gas and condensate of deposits of this region is the very high content of nitrogen ([1], see Table 1). Transportation of such gas without preliminary removal of nitrogen on pipelines is economically unreasonable because of low temperature of condensation of a mix (connected with the presence of a plenty of nitrogen) and expenses on compression and transportation of inert components.

At the same time, the unique peculiarity of the gas deposits is the high content of helium, reaching up to 0.5%. Considering a high market price of helium in the world, it is advantageous to isolate helium from natural gas using cryogenic technique on-site. In this case the hydrocarbon components of natural gas would be separated from undesirable gases (CO_2, H_2O, N_2). The final product from installations of low-temperature separation of helium is a dry hydrocarbon mixture (or liquefied natural gas (LNG)) depending on the ways of cold-conservation on the process. LNG can further be delivered to the consumers using pipelines or cryogenic capacities. Another possibility is to convert components of LNG to valuable products on-site.

It was shown that oxidative coupling of methane (OCM) appeared a very promising new method for the production of ethylene. The main problems which restrict the industrial application of the process is relatively low concentration of ethylene in output

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Table 1
The average composition of natural gas and mixture of hydrocarbons after removal of inert components

Component	Composition (%)	
	Natural gas	Hydrocarbons
Nitrogen	15–27	—
CO_2	<0.2	—
Helium	0.5	—
Methane	63–89	90.6–92.3
Ethane		5.1–6.4
Propane	7–12.5	1.6–2
C_4^+		0.9

gases and large amount of heat evolved. The possible way to overcome these restrictions is to combine OCM process with a heat consuming chemical reaction, for example dehydrogenation of ethane. This reaction increases C_2H_4 content in products and consumes some heat preventing from overheating. Calculations made previously [2] have shown that the combined process "OCM – ethane dehydration" can be considered as an alternative to the cracking processes of ethylene production. The aim of the present study is to apply this approach to the natural gas deposits of Krasnoyarsk region taking advantage of using LNG as a starting material.

2. Experimental

The flow sheet of the process design for OCM combined with ethane dehydrogenation is shown in Fig. 1. An important feature of the process is the utilisation of LNG to cool outlet stream to (−150°C)–(−160°C) after separation of CO_2 and H_2O (heat exchanger H_3). The cool mixture is separated into liquid and gas phases in flash drum F1 according to its temperature, pressure (normally 101.3 kPa) and initial composition. Gas phase containing mainly CO, H_2 and a fraction of unreacted methane is purged, liquid phase enters demetaniser to separate CH_4 and C_2^+ products. Methane obtained is recycled and C_2^+ comes into the ethylene fractionator to separate ethylene (a final product) and ethane+C_3^+ mixture which is also

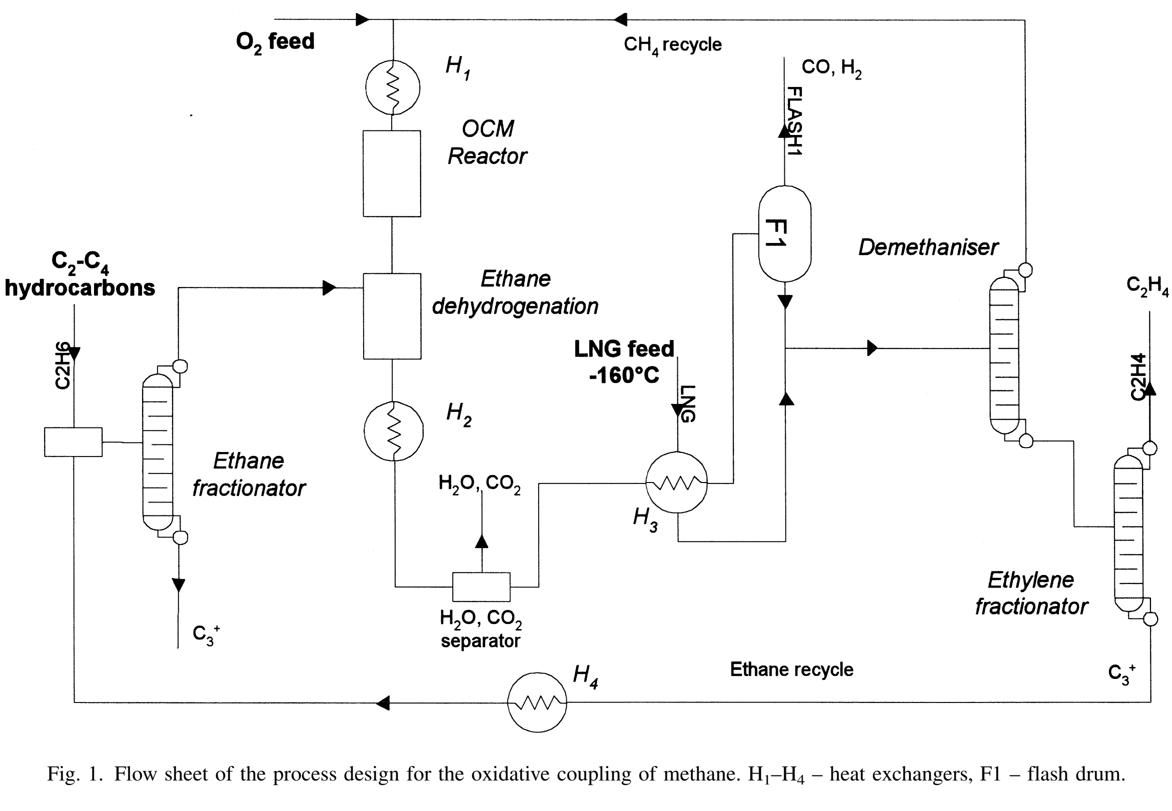

Fig. 1. Flow sheet of the process design for the oxidative coupling of methane. H_1–H_4 – heat exchangers, F1 – flash drum.

recycled. Calculation of the heat balances and phase equilibrium was based on available thermodynamic data for C_1–C_4 hydrocarbons and inorganic compounds [3]. Soave–Redlich–Kwong equation-of-state was used to predict the behaviour of mixtures.

To model OCM reactor a data of laboratory test of an average performance catalyst is assumed. It operates at 800–850°C ($CH_4:O_2=85:15$, $P=101.3$ kPa) and gives 25% conversion of methane with 66% C_2^+ selectivity according to the reaction (1). Under condition studied total conversion of oxygen is observed. The reactor of ethane dehydrogenation operates on the energy produced in the OCM reactor. It can be either a separated reactor or one integrated into the coupling reactor. Conversion of ethane is assumed to be 60% and selectivity 82% (by product is methane) according to the reaction (2).

$$20.4CH_4 + 15.98O_2 = 1.63C_2H_6 + 5.06C_2H_4 + 4.46CO_2 + 20.48H_2O + 5.31H_2 + 2.56CO \quad (1)$$

$$50C_2H_6 = 41C_2H_4 + 32H_2 + 18CH_4 \quad (2)$$

On the basis of process flow diagram material balance has been estimated for different cases. The parameters to be varied are temperature of flash drum F1, ethane input flow and temperature (T_1) of the CH_4–O_2 mixture entering the reactor of OCM (temperature of output gases leaving preheater H_1). Simulation runs were performed as follows: LNG flow, temperature of F1 and temperature T_1 were kept constant and the flow of ethane was varied until the amount of heat evolved in reaction (1) became equal to that consumed in reaction (2) plus heat required to increase the temperature of methane–oxygen mixture from T_1 to 850°C (temperature of OCM reaction).

3. Results

Simulation shows that the amount of heat evolved for conditions under study is greater than that required to convert all C_2H_6 from LNG (about 6%) to C_2H_4 and therefore it is possible to produce an extra amount of ethylene by dehydrogenation reaction of added ethane. A result of typical simulation is shown in Table 2. The data given in the table correspond formally to the 100% conversion of C_2H_6 to C_2H_4 and 52% selectivity of conversion of methane to ethylene (14% yield per feed CH_4). As far as ethylene can be formed from OCM and C_2H_6 dehydrogenation it is interesting to study the influence of process parameters on the amount of C_2H_4 formed from methane. It is found that the main factor which determines the performance of the process is temperature of flash drum F1. The lower the temperature of F1, the larger the amount of recycled CH_4. The variations of yield and selectivity of ethylene formation as a function of temperature of F1 are shown in Fig. 2(a) and (b).

The data given in Fig. 2 show that selectivity and yield of ethylene formation from methane can reach the values of 58% and 34% correspondingly depending on the F1 temperature. Obviously, this effect is due to methane recycling and therefore for the given process design high yield of C_2H_4 can be reached even with a moderate performance catalyst of OCM.

Another important factor for the overall performance is temperature of gases leaving preheater H_1. As a rough estimation it corresponds to a different degree of conservation of heat, evolved in reaction of OCM. The lower the temperature of H_1 is, the less amount of ethane can be additionally dehydrogenated because heat of the reaction is consumed on increasing the temperature of reactants. As can be seen from the data given in Fig. 2 the decrease of preheater

Table 2
Typical flows of C_1–C_2 hydrocarbons and hydrogen used to calculate flow sheet (Fig. 1). Temperature of preheater 400°C, flash F1 at −158°C

	Input streams[a] (kg mol/h)		Outlet streams (kg mol/h)	
	C_2H_6	LNG	FLASH1	C_2H_4
Methane	—	91.0	66.5	—
Ethane	13.3	6.0	<0.1	—
Ethylene	—	—	0.2	25.7
Hydrogen	—	—	22.4	—

[a]Flow of oxygen is calculated according to the stoicheometry of reaction (1) with 0.1% weight excess.

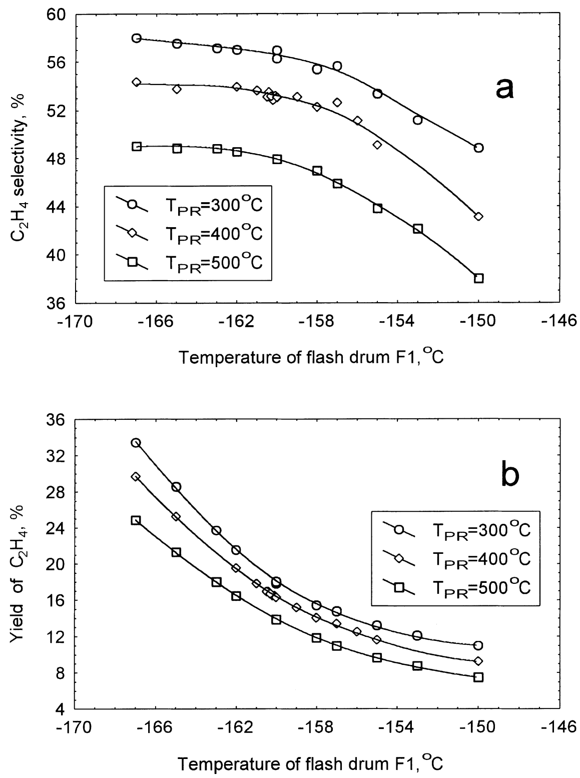

Fig. 2. Calculated influence of temperature of flash drum F1 on selectivity (a) and yield (b) of ethylene formation from methane. T_{PR} – temperature of output gases of preheater H_1.

temperature leads to increase both selectivity and yield of ethylene formation.

It is known that substantial part of the energy required for the process is consumed on compression/cooling of circulating gases. Our calculation shows that this amount can be greatly reduced if one uses LNG as a starting material. Fig. 3 shows the difference of the specific heat duty to cool recirculating gases for two variants: (i) cold of LNG is used to cool recirculating gases and (ii) natural gas is mixed with liquid phase of flash drum F1. It is obvious that depending on the F1 and preheater temperatures, the difference reaches from 1.5 to 5 times. This indicates that the process of treatment of natural gas including helium removal – LNG conversion to ethylene by OCM reaction – is a possible alternative to traditional methods of gas treatment. The main problems that obstacle its introduction are the OCM reactor design, and selection of the proper materials for OCM reactor and cryogenic equipment.

4. Conclusions

1. For the given process design high yield of C_2H_4 can be reached even with a moderate performance catalyst of OCM.
2. The use of liquefied natural gas allows to reduce energy requirements to cool recycled streams.

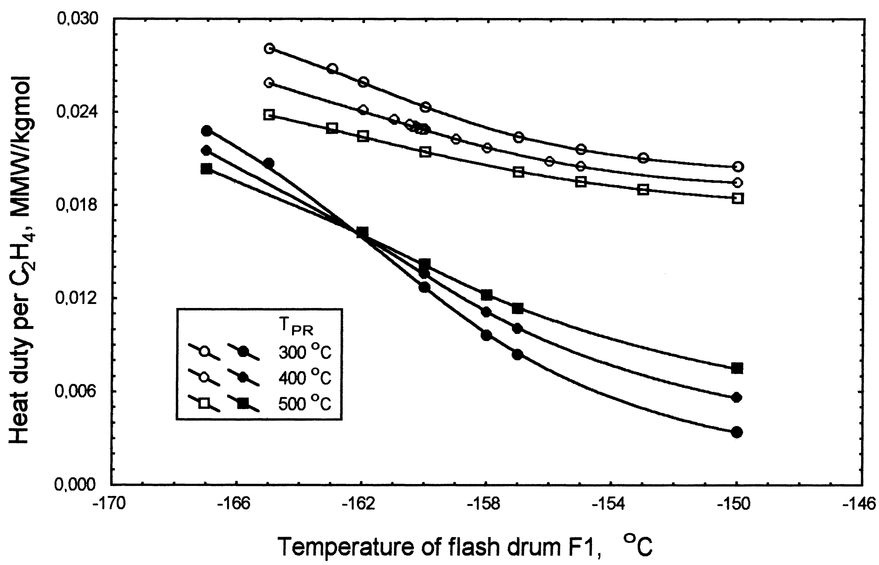

Fig. 3. Calculated influence of temperature of flash drum F1 on specific heat duty: Open symbols – LNG is by-passed heat exchanger H_3; closed symbols – LNG through H_3.

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