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MODELING OF A REACTOR PREPARATION ETHYLENE FROM METHANE

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Abstract

In this study, catalytic oxygenation of methane and the influence of various factors in the process of ethylene production were studied. Based on the results obtained, the optimal conditions and the structure of the catalyst were chosen : (Mn2O3)x · (Na2MoO4)y · (ZrO2)z. The process was thermodynamically evaluated to obtain the most appropriate technology for extracting ethylene from methane, and the effect of various technological parameters on its main characteristics for mathematical modeling of the reactor was investigated.

***Keywords:** temperature; bulk velocity; adiabatic reactor; contact time; conversion; diameter; film thickness; mass transfer.*

Introduction

Uzbekistan has vast reserves of oil and natural gas. Natural gas and oil are known to be reserves of non-renewable and limited raw materials. The rational use of oil and gas will help develop the chemical industry at a higher level. Particular attention is paid to the use of highly efficient, low-waste, economical, environmentally friendly technologies and environmental protection for the efficient use of oil and natural gas. Based on the foregoing, one of the main challenges facing the scientists of the world is the introduction of new methods of producing sync. Tactical materials important for the national economy, which can replace products imported on the basis of local raw materials and industrial waste, and without waste, environmentally friendly, high-quality and competitive. The development of new technologies, At the same time, the only reasonable way to process natural gas is through oxygenation. This process occurs at one stage and at atmospheric pressure. This process passes through ethane and ethane is dehydrated with ethylene production. Considering the whole substance, you can write the following sequence of reactions.

$$400CH4+259O2 \rightarrow 90C2H6+70C2H4+64CO2+374H2O+16H2+16CO$$

$$\Delta H_{800^0 C} = -514 \text{ kJ/mol.}$$

Experimental

The gaseous products of the reaction was analyzed using a “Gazokhrom3101” thermochemical detector using the following thermostat: Thermostat temperature is 100°C, transport gas (air) flow rate is 35 ml/min, the length of the column filled with activated carbon is 1 m, internal diameter is 3 mm. Quantitative analysis was carried out by the absolute rating method. The

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catalytic activity of more than 10 catalysts was tested for the reaction of methane oxygenation. As is known, manganese-based catalysts have high catalytic activity and selectivity in the process of ethylene oxidation with methane. Therefore, we learned that manganese-based catalysts are a promoter feature of various compounds. The results are shown in the **TABLE 1,**below.

TABLE 1. **Results of studying the promoting properties of various compounds in catalysts prepared from manganese.**

Serial No	Promoter	Reactor temperature, °C	Methane conversion, mol, %	Selectivity, %		Efficiency of ethylene, %
				C_2-hydrocarbons	ethylene	
1	Na_3PO_4	700	14,6	100	58,0	8,5
		750	24,7	100	63,4	15,8
		800	38,8	93,9	70,0	27,3
2	$Na_2B_4O_7$	700	15,6	65,7	48,7	7,6
		750	23,2	55,0	68,1	15,8
		800	35,6	37,7	76,1	27,1
3	Na_2MoO_4	700	11,3	100	64,7	11,2
		750	28,0	100	70,1	19,8
		800	43,0	100	76,5	32,9
4	Na_2WO_4	700	13,8	60,3	49,3	6,8
		750	21,5	28,8	65,6	14,1
		800	32,9	29,9	69,3	22,8

As can be seen from the TABLE 1, when Na2MoO4 is added to the manganese catalyst, the total conversion of methane is 43.0% at 800 ° C, 32.9% of the efficiency ethylene and 76.5% ethylene selectivity. We then added d-metal compounds to Mn2O3 · Na2MoO4. The best results were obtained by adding a catalyst ZrO2. The results of the experiments are shown in **TABLE 2.**

TABLE 2. **The effect of the catalyst on methane activity in the oxidative condensation reaction.**

Serial No	Composition of catalyst	Methane rotation level, %		Selectivity, %
		Common	C_2H_4-a	
1	La_2O_3	42,2	28,6	67,8
2	PbO_2	46,4	29,7	64,0
3	KCl	40,9	28,6	70,0
4	KBr	37,1	21,2	57,1
5	ZrO_2	52,6	42,8	81,4
6	BeO	48,2	34,6	71,8

The introduction of the ZrO_2 catalyst had a positive effect on its activation. When added ZrO2 catalyst, the efficiency of ethylene increased from 32.9% to 42.8% and the selectivity to ethylene from 76.5 to 81.4% respectively. Further experiments

(Mn2O3) x· (Na2MoO4) y (ZrO2) z with the participation of an optimal catalyst were carried out. The conversion of methane depends on the C2-hydrocarbon process, depends on the catalytic composition used, but also depends on the reaction conditions (temperature, methane, air, specific bulk velocity). Thus, we learned the effect of various factors on the reaction rate. The bulk velocity was investigated at a temperature of 800°C and a ratio of CH4: air=1: 2. The change in bulk velocity was achieved by changing the size of the catalyst, which must be applied to the reactor. The first methane-air mixture was sent continuously. The results are shown in **TABLE 3.**

TABLE 3. **Effect of bulk velocity on methane oxygenation.**

S.No	Magnitude of bulk velocity, h^{-1}	Catalyst volume, ml	Conversion rate		S %
			General	to C_2H_4	
1.	600	10,0	68,5	28,6	41,8
2.	800	7,5	61,9	35,8	57,8
3.	1000	6,0	52,6	42,8	81,4
4.	1200	5,0	43,3	32,9	75,9
5.	1400	4,2	34,8	23,6	67,8

However, it was noted that additional products are formed (decomposition of ethylene). The optimal value of the bulk velocity is 1000 h -1, the value of ethylene is 42.8%, and the selectivity is 81.4%. The effect of temperature on the methane oxidation reaction was investigated at constant bulk velocity (1000 h-1) and methane: air=1: 2 with the presence of a catalyst of optimal composition with a range of 50°at intervals of 600-850°C. The results are shown in **TABLE 4.**

The temperature of methane has a significant effect on the oxidation reaction, as shown in **TABLE 4.**

Production of ethylene starts at 600˚C. The highest ethylene yield was observed at 800°C. Increasing the temperature from the optimum temperature can degrade the process. Therefore, the ethylene content and selectivity decrease.

TABLE 4.**The effect of temperature on the methane oxygenation reaction.**

S.No	Temperature, ºC	Methane conversion, mol, %		Selectivity,%
		General	C_2H_4 a	
1.	600	15,0	следы	-
2.	700	36,4	23,4	64,3
3.	750	45,6	33,2	72,8
4.	800	52,6	42,8	81,4
5.	850	58,0	36,5	63,0

The effect of methane: air with temperatures of 800°C and a bulk velocity of 1000 h^{-1}. The results are shown in TABLE 5.

The results of the **TABLE 5,** show that when the amount of air in the compound increases, methane conversion increases, ethylene efficiency and selectivity decrease.

TABLE 5. **Results of studying the effect of methane-air ratio for methane oxygenation. (T=750OC, Vcat=6 ml).**

S.No	Methane : air	Methane conversion rate, %		Selectivity ,%
		General	to C_2H_4	
1.	3:1	25,0	6,2	24,8
2.	2:1	32,4	12,5	38,6
3.	1:1	45,8	23,6	51,5
4.	1:2	52,6	42,8	81,4
5.	1:3	60,8	30,5	50,2

To study the kinetic regularities of the methane oxygenation reaction, the effect of methane and oxygen partial pressure on the rate of production of ethylene at a temperature of 700 ÷ 800°C and a bulk velocity 600 ÷ 1200 h-1. In studying the effect of the partial pressure of the reactants on the process flow laws changed the partial pressure of the gas and left the latter unchanged. In order not to change the linear rate, the required amount of argon gas was sent to the reaction zone. The catalyst size was adapted to the specific velocity test conditions for permanent storage.

The Results of the Experiment and their Discussion.

Thermodynamic evaluation of the process and mathematical modeling of the reactor, which is the core of the technological process, plays an important role in creating development technologies.

Thermodynamic analysis of the methane oxygenation reaction:

Thermodynamic parameters of the reaction, calculated on the basis of the values of heat and Gibbs energy, are given in **TABLE 6**.

TABLE 6. **Calculated values of heat and Gibbs energy of the reaction.**

S.No	Reaction	ΔH^0_{298}; kJ/mol	ΔG^0, J/mol · K
1	$4CH_4+O_2 \rightarrow 2C_2H_6+2H_2O$	-176,6	-197,296
2	$2C_2H_6+O_2 \rightarrow 2C_2H_4+2H_2O$	-104,7	-363,242
3	$2CH_4+O_2 \rightarrow C_2H_4+2H_2O$	-281,314	-280,06
4	$C_2H_4+2O_2 \rightarrow 2CO+2H_2O$	-756,162	-937,574
5	$CH_4+2O_2 \rightarrow CO_2+2H_2O$	-801,724	-1006,544
6	$C_2H_4+3O_2 \rightarrow 2CO_2+2H_2O$	-1321,716	-1286,186
7	$CH_4+1,5O_2 \rightarrow CO+2H_2O$	-518,738	-609,026

The adiabatic heating of the gas mixture is an important characteristic of the reactor. The adiabatic heating of gases for different values of the methane-oxygen ratio based on the heat balance of the catalyst bed was calculated using the formula:

$$Wenter\Sigma\left(C_i enter \cdot H_i^{Tlayer}\right) - Wenter\Sigma\left(Cexit \cdot H_i^{Tlayer}\right) = Wenter \cdot \int_{T_g^0}^{Tlayer} \Sigma\left(Center \cdot C_{p,i}^T\right) dT$$

The calculation results are shown in **FIG. 1,** below.

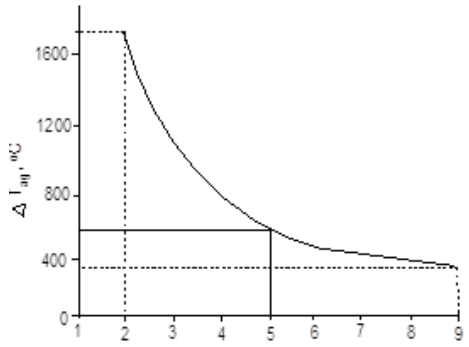

FIG. 1. **Relationship between the ratio of CH_4:O_2 and adiabatic heating on the source gas at p = 0.1 MPa.**

As can be seen from the figure, methane content increases with adiabatic heating. As can be seen from the **TABLE 7,** when $Na2MoO4$ is added to the manganese catalyst, the total methane conversion is 43.0% at 800°C, 32.9% of the efficiency of ethylene and 76.5% selectivity ethylene. In terms of the ratio of methane-oxygen adiabatic heating to 575°C.

When the methane content in the source gases is 90%, adiabatic heating decreases to 325°C. As it is known, adiabatic type reactors are often used for carrying out catalytic processes, while the selectivity of the processes varies widely in the temperature range. The advantage of these reactors is that 2-3 t/m^3 metal tanks (at times) are smaller and easy and cheap to manufacture. Its disadvantage is that the reactions are carried out with a large thermal effect, and the selectivity in the catalyst layer is not the same to a high approximation, methane oxygenation reaction may be carried out for 4-5-stage device. Under these conditions, this process is a good way to work.

TABLE 7. **Parameters on the process are 5-step adiabatic reactor Mathematical modeling of methane oxygenation reactor**

P, MPa	**CH_4/O_2 mol**	**T_{input},°C**	**T_{output},°C**	$\sum S$	K_{O_2} %	K_{CH_4},%	**Yield**	
							C_2	**C_2H_4**
0,1	5	800	1000	0,13	95,6	44,8	43,2	40,3

The ideal isothermal reactor model for reactor simulation was used:

The limiting stage of the process in the extraction of methane is the diffusion of oxygen on the outer surface. The oxygen concentration and the partial pressure on the particle surface were in the following equation: $\beta(C_{O_2}^b - C_{O_2}^S) = R_{O_2}^S$ The change in the total pressure on the layer is expressed by the Ergan equation: $\frac{\Delta P}{L} = f\frac{\alpha}{\varepsilon^2}\frac{\rho \cdot U^2}{2}$.

The coefficient of hydraulic resistance for colored particles was determined by the following formula: $f = \frac{38,4}{\mathrm{Re}} + 0,586$ in this $\mathrm{Re}_э = \frac{4u}{\nu_{арал} \cdot \alpha}$. In the automatic mode, all the heat dissipated during the process is used to heat the unwanted gas.

Therefore, the temperatures of the incoming and outgoing reactors are governed by the heat transfer equation (8) of the catalyst.

As a result of studying the effect of mass transfer coefficients and other factors on the process parameters, the main indicators of the oxidizer of methane oxidizer were determined. The results are given in **TABLE 8.**

Thus, methane oxygenation can be carried out in a single-stage adiabatic reactor in an auto thermal mode with an effective diameter of catalyst particles under external diffusion conditions of 5.0 mm and a linear rate of 0.36 m/s. The specific performance of the catalyst in the amount of C_2 hydrocarbons in the selected mode is 17,280 kg $(C_2)/m^3 \cdot$ hour (in ethylene - 16253.5 kg/m3 · hour). The thickness of the catalyst layer is 2.0 cm. Thus, the capacity of the ethylene block is 16253.5 thousand units. kg/year, the specific consumption of methane is 360 $nm^3/m^2 \cdot$ hour.

TABLE 8. **The Main Indicators of the Oxidizer of Methane Oxidizer were Determined.**

Parameter	**ACM**
Characteristic particle size d_ρ, mm	5.0
Layer thickness, h, m/sec	2.0
Gas speed, u, m/sec	0.36
Conditional contact time τ, sec	0.13
Conversion , X, %	95.6
Macrokinetic speed constant's, ω, c^{-1}	36.7
Mass transfer coefficient, β, c^{-1}	44.0
Kinetic speed constant's, k, c^{-1}	220.0
Constant relation, k/β	5.0
Specific yield to C_2, g $g/m^3 \cdot$hour	1.9

TABLE 9. **Construction characteristic of the methane oxygenation reactor (ACM).**

Main characteristics of the reactor	**Values**
Capacity to C_2(ethylene), thousand kg/year	17280.0(1616253.5,0)
Diameter of the device, m	7.9
Specific methane consumption, $nm^3/m^2 \cdot h$	380
Oxygen concentration, vol%	16253.5

It should be noted that the power of methane oxygenation reactor can be increased by increasing the pressure in the system. For example, when the pressure increases to 0.5 MPa, the specific power of the methane oxygenation reactor is about 33.800 Kg/year. The main construction characteristics of the reactor are shown in **TABLE 9.**

Conclusion

1. The catalytic oxygenation of methane and the influence of various factors on the process of ethylene production were investigated.

2. The process was thermodynamically evaluated, and a mathematical model of the reactor was modeled.

3. The basic parameters and design characteristics of the reactor (RCM) have been studied.

4. It was found that catalytic oxygenation of methane facilitates the process of producing ethylene in a 5-stage adatomic reactor.

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