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To cite this article: S V Afanasiev et al 2018 IOP Conf. Ser.: Mater. Sci. Eng. 450 062002

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Combined production of ammonia and methanol as the way to deal with the greenhouse gas

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Abstract. Technological processes in the energy sector and at the enterprises of nitrogen fertilizers, accompanied by the release of large amounts of greenhouse gas - carbon dioxide into the atmosphere are considered. Optimal options for its utilization are proposed, based on the bicarbonate conversion of natural gas to produce methanol and gas-cyclic CO₂ injection into oil producing wells in order to increase oil recovery.

1. Introduction
Improving the technology and equipment for large-scale carbon dioxide production is a priority for any major manufacturer of ammonia and urea. This is because carbon dioxide is widely used not only in large-scale chemistry enterprises, but also in various industries, including petrochemistry. The growth of its consumption is promoted by the creation of large aggregates with carbon dioxide conversion, on which carbon dioxide is used as one of the components of industrial synthesis.

At the same time, it must be admitted that carbon dioxide is a greenhouse gas and climate warming on our planet is associated with its content in the atmosphere. Incineration or conversion of methane produces an equal amount of carbon dioxide. Its emissions from many large combined heat and power plants exceed 10 million tons per year.

For this reason, the largest producers of carbon dioxide are heat and power plants and factories producing methanol and nitrogen fertilizers.

By the order of the Government of the Russian Federation No. 504-p dated April 2, 2014, an Action Plan was drawn up to ensure the reduction of greenhouse gas emissions by 2020 to a level of no more than 75 % of these emissions in 1990.

Introduction of payments in the amount of US $ 50-80 per ton is considered as effective measures to reduce carbon dioxide emissions, which can lead to the shutdown of a number of gas chemistry enterprises.

In our opinion, as a promising method of processing liquid carbon dioxide, its gas-cyclic injection into oil-bearing formations should be considered with the aim of intensifying oil production.

This ensures a reduction in energy costs, the elimination of the risk of formation of gas hydrates, increased oil recovery from fields with high-viscosity oil.

It is known that after the flooding of oil fields using conventional technology or using their improved options (cyclical effect, changing the direction of fluid flow, water-gas cyclic effect), or with increasing displacing properties of water (surfactants, polymers, alkalis) in the depths remain undetectable until 30 – 70 % of the initial oil reserves.

Residual oil can be displaced only by those working agents that are mixed with oil and water or have ultra-low interfacial tension at the interface. Such conditions arise when high-viscosity oil is forced out
by carbon dioxide.

The main thing in the application of these methods is to provide a high coverage of the oil reservoir with an effective displacing agent (carbon dioxide) and a micellar solution.

When carbon dioxide is dissolved in water, its viscosity slightly increases, but this increase is insignificant. With mass content in water 3 – 5 % of carbon dioxide increases the viscosity of the oil at 20 – 30 %. The resulting carbonic acid dissolves formation rocks and increases permeability. In the presence of carbon dioxide, the swelling of clay particles is reduced. CO₂ dissolves in oil 4 to 10 times better than in water, so it can pass from an aqueous solution to oil.

Carbon dioxide in water contributes to the rupture and washing of the film of oil covering the grain of the rock, and reduces the possibility of rupture of the water film. В результате масляные капельки с малым межфазным натяжением свободно движутся в пористых каналах.

According to research data, CO₂ is dissolved in oil much better than methane and its gaseous homologues, and the solubility increases with increasing pressure and molecular weight of oil. Contacting with oil, carbon dioxide partially dissolves in it and simultaneously extracts hydrocarbons, enriching them. As a result, the pressure required for the mixed displacement of oil by carbon dioxide is three times less than one hydrocarbon gas.

This paper discusses the technological aspects of the production and processing of carbon dioxide on the example of PJSC "Togliattiazot".

2. Features of CO₂ emission from gas mixtures in absorption / desorption processes

To extract CO₂ from the gas mixture, absorption and desorption processes are used.

The production of CO₂, which focuses on ammonia plants, implements two classical schemes for its separation from natural gas conversion products: ethanolamine and using potash solution. The first method, as is known [1], is described by two main chemical reactions:

\[
2RNH₂ + H₂O + CO₂ \leftrightarrow (RNH₃)₂CO,
\]

(1)

\[
(RNH₃)₂CO₃ + H₂O + CO₂ \leftrightarrow 2RNH₃HCO₃,
\]

(2)

where \( R = HOCH₂CH₂ \).

Equations (1) and (2) are a simplified model for the absorption of carbon dioxide by ethanolamines, the final products of which are carbonates and ethanol ammonium bicarbonates.

At a temperature of 35-45 °C, these reactions go to the right (absorption), and at a temperature of 105 °C and above - from right to left (desorption).

A detailed consideration of the mechanism of interaction of CO₂ with ethanolamines allows us to establish that at relatively low degrees of carbonization (\( \alpha < 0.5 \) mol CO₂ per mole of a monoethanolamine derivative), the reaction proceeds with the formation of substituted carbamic acid:

\[
CO₂ + RNH₂ \leftrightarrow RNHCOO⁻ + H⁺.
\]

(3)

In this case, an acid-base equilibrium is instantly established in an aqueous solution:

\[
RNH₂ + H⁺ \leftrightarrow RNH₃⁺.
\]

(4)

The final product of reactions (3) and (4) becomes a carbamate of the following structure:

\[
RNH₂COO⁻ + RNH₃ \leftrightarrow RNHCOORNH₃.
\]

(5)

The total reaction of the interaction of CO₂ with an ethanolamine molecule by the carbamate mechanism can be written as:

\[
(1 + \gamma)RNH₂ + CO₂ \leftrightarrow (1 - \gamma)RNHCOOH + \gamma RNHCOO⁻ + \gamma RNH₃⁺.
\]

(6)

A significant drawback of the monoethanolamine method of purifying gas mixtures from CO₂ is the formation of significant amounts of resinous substances due to the cyclization of monoethanolamine into oxazolidone-2 derivatives and further into the products of their transformation. Thanks to our efforts, effective methods were found to process this waste into a filler for paints and varnishes,
surfactants, and a hardening accelerator for polyisocyanate compositions [2].

Of particular interest is the amine modifier of urea-formaldehyde resins, synthesized from the cubic residue of monoethanolamine purification of ammonia production. It is manufactured by PJSC “Togliattiazot” according to technical conditions 2423-017-00206492-2002. The modifier is a mixture of oxazolidine-2 derivatives and compounds with the general formula R-CH₂CH₂OH, taken in a specific ratio [3]. In order to increase the efficiency of carbon dioxide emission from gas mixtures, most enterprises producing mineral fertilizers are replacing monoethanolamine with methyldiethanolamine. At the same time, the separator is excluded from the technological scheme, the consumption rates of raw materials and energy carriers for output are reduced.

The second common method of purification of ammonia from carbon dioxide is associated with the use of an aqueous solution of potash mainly in Kemico-type aggregates. It is described by the following kinetic model:

$$K_2CO_3 + H_2O + CO_2 \leftrightarrow 2KHCO_3.$$  \hspace{1cm} (7)

At a temperature of 45-55 °C, reaction (7) goes to the right, i.e. CO₂ absorption is observed; at a temperature of 102 °C and higher - to the left (desorption).

In parallel with this reaction, electrolytic dissociation of $K_2CO_3$ and $KNSO_3$ proceeds, described by equations (8) and (9):

$$K_2CO_3 + H_2O \leftrightarrow 2K^+ + HCO_3^- + OH^-,$$  \hspace{1cm} (8)

$$KHCO_3 + H_2O \leftrightarrow K^+ + H_2CO_3 + OH^-.$$  \hspace{1cm} (9)

The first stage of hydrolysis is characterized by the existence of an equilibrium between the CO₃²⁻ and HCO₃⁻ ions, and the second between the HCO₃⁻ ions and the H₂CO₃ molecules.

In order to increase the efficiency of the absorption and desorption processes, diethanolamine and a $V_2O_5$ corrosion inhibitor are added to the potash solution. These components in aqueous solution have the following content: $K_2CO_3$ - 24-30 %; diethanolamine - 2.0-3.5 %; $V_2O_5$ - not less than 0.4 % (“Benfield” solution).

The volumes of carbon dioxide production of various degrees of purity in PJSC “Togliattiazot” are characterized by tables 1 and 2.

**Table 1.** “Dirty” carbon dioxide production.

| Plant | Units of measure | Volume of issue |
|-------|-----------------|-----------------|
| №1   | kg / h          | 46532           |
|       | tons / year     | 372263          |
| №2   | kg / h          | 44152           |
|       | tons / year     | 353213          |
| №3   | kg / h          | 39013           |
|       | tons / year     | 312108          |
| №4   | kg / h          | 41334           |
|       | tons / year     | 330672          |
| Total |                 | 1368000         |

**Table 2.** Production of “pure” carbon dioxide.

| Plant | Units of measure | Volume of issue |
|-------|-----------------|-----------------|
| №5   | kg / h          | 35501           |
|       | tons / year     | 284008          |
| №6   | kg / h          | 41605           |
|       | tons / year     | 332842          |
| №7   | kg / h          | 34995           |
|       | tons / year     | 279946          |
| Total |                 | 1200000         |
The balance of CO$_2$ consumption can be illustrated by the following data. “Dirty” CO$_2$ is used in a liquid carbon dioxide plant. The line operates periodically and consumes about 150 thousand tons during the year. In addition, hydrogen dioxide-contaminated carbon dioxide is used in the production of methanol with a shortage of pure fraction in the amount of 18-20 tons / h. per one unit with a capacity of 400 thousand tons / year.

A large consumer of “pure” CO$_2$ is the production of urea, which accounts for about 640 thousand tons / year. Another 300 thousand tons / year is spent on carrying out carbon dioxide conversion on two methanol production units.

To date, the company’s reserve has about 500 thousand tons of carbon dioxide per year, which can be used for gas-cyclic injection into oil producing wells. The process technology was developed by the authors of this article and is in the process of patenting.

3. Production of liquid low-temperature CO$_2$

At present, progressive and energy-intensive methods of carbon dioxide liquefaction have been proposed, one of which is described by G.K. Lavrenchenko, A.V. Kopytin, S.V. Afanasyev [4].

In the case of PJSC “Tolyattiazot”, the enterprise mastered the production of liquid low-temperature CO$_2$, which is carried out in the following sequence.

Carbon dioxide from the factory collector enters the separator to separate the acidic condensate from the source gas. Then it is sent to the suction in a two-part, four-stage centrifugal compressor, where it is compressed to a pressure of 35 kgf / cm$^2$. After compression, after passing through another separator, carbon dioxide is fed to the drying system. It consists of two adsorbers filled with two layers of silica gel of grades KSKG and KSMG. The moisture control of the dried gas is controlled by a device of the “Baikal-2V” type. Adsorbers work alternately in automatic or semi-automatic modes according to the program in two cycles: “adsorption” and “regeneration”.

Dried CO$_2$ gas with a temperature of 5-10 °C and a dew point no higher than minus 38 °C enters 1 condenser. Condensation of carbon dioxide is carried out in the tube space of the apparatus at temperatures from minus 5 to minus 20 °C due to cooling of CO$_2$ by freon entering the annular space. Liquid carbon dioxide from a condenser with a temperature of from 0 to minus 15 °C and with a pressure of 30-35 kgf / cm$^2$ is discharged into a storage tank.

Non-condensed gaseous carbon dioxide is fed to a catalytic purification unit to produce CO$_2$ of high quality used for special needs. First, the gas passes a carbon filter, where it is purified from organic impurities and sent to the oxidation reactor of carbon monoxide and hydrogen to carbon dioxide and water on a ruthenium-palladium catalyst. Oxidation proceeds according to exothermic reactions (10) and (11):

\[
2CO + O_2 \leftrightarrow 2CO_2 + Q_1, \quad (10)
\]
\[
2H_2 + O_2 \leftrightarrow 2H_2O + Q_2. \quad (11)
\]

The temperature in the catalytic reaction zone is maintained at 220-240 °C. To speed up the oxidation process, the gas in front of the reactor is heated in a heat exchanger to a temperature of 120 °C. Purified carbon dioxide leaving the apparatus is cooled, the separator passes and is sent for drying to silica gel adsorbers. Dried CO$_2$ gas is condensed at a pressure of 28-35 kgf / cm$^2$ in the temperature range from minus 5 to minus 20 °C due to evaporation of liquid freon supplied to the annulus of the condenser from the refrigeration unit. Liquid carbon dioxide is collected in the collection, and the residual and purge gases are discharged into the atmosphere.

4. Pair - carbon acid gas conversion with methanol recovery

The literature describes various methods for producing methyl alcohol, including the reaction of carbon oxides with hydrogen under pressure of 1.0–15.0 MPa, a temperature of 160–300 °C, a space velocity of 7,000–25,000 h$^{-1}$ in the presence of a catalyst containing oxides of copper and zinc, separation of methanol from the reaction mixture and recycling of unreacted substances in the synthesis of methanol.
[5]. A mixture of hydrogen with oxide and carbon dioxide is used as a raw material, in which the CO₂ content varies in the range of 3–12 vol. %. In the reaction gas in contact with the catalyst, the volume ratio of hydrogen to the sum of carbon oxides is 1.3–3.0 times the stoichiometric one.

The main disadvantages of the known processes include the reduced specific performance of the copper-zinc catalyst, as well as the high energy costs of recirculation of the gas mixture.

The study was aimed at improving the technological scheme of the process while maintaining a high level of its effectiveness.

It is well known that the processing of synthesis gas with a carbon monoxide content of more than 30 vol. % and nitrogen over 40 vol. % is uneconomical. For this reason, the proposed method uses synthesis gas, in which the dosage of CO is maintained below 25 vol. %, and the volume ratio of H₂ / (CO + CO₂) is in the range from 2 to 5.

To achieve the optimum concentration of CO₂, its feed to the reformer can be used, or the feed of the converted gas with pure carbon dioxide can be used.

The limit of the upper limit of CO₂ in the synthesis gas is 10 vol. % due to the possibility of reducing the rate of formation of methanol with a higher content of carbon dioxide in the gas mixture.

Figure 1 shows a schematic diagram of the proposed process.

![Figure 1. Technological scheme for the production of methanol with CO₂: 1-compressor; 2-air cooler; 3-separator; 4-flow reactor; 5-recuperative heat exchanger; 6-fridge-condenser; 7-separator; 8-recuperative heat exchanger; 9-catalytic reactor; 10-inline heat exchanger; 11-refrigerator-condenser; 12-refrigerator-condenser.](image)

The converted gas from the reforming furnace is fed to the suction side of the compressor 1, is cooled by an air cooler 2 and is sent to the separator 3 to separate the moisture. The dried synthesis gas is compressed to a predetermined pressure and is divided into two parts. The first (stream A) is in contact with the catalyst in the flow reactor 4 and at the outlet of it releases heat to the regenerative heat exchanger 5 and the condenser-condenser 6. The condensed methanol - raw material is separated in the separator 7.

In turn, the second part of the converted gas (stream B) is mixed with circulating gas, heated in a recuperative heat exchanger 8 and fed to a horizontal type 9 catalytic reactor with an integrated heat exchanger 10. The resulting methanol-containing gas mixture releases the reaction heat to the air cooler 11 and the condenser-cooler 12 and sent to the separator 7 for the separation of methanol.
5. Conclusion

On the example of a large chemical enterprise focused on the production of mineral fertilizers, the issues of production and processing of carbon dioxide were considered.

It is shown that the increase in carbon dioxide production capacity should be accompanied by the solution of two questions: the organization of production for deep processing of CO₂ and its use in oil-producing enterprises.

The introduction of such projects in Russia will help to solve two problems: on the one hand, the technology will increase oil recovery at late stages of development, which is especially important due to the deterioration of reserves structure and deficiencies in exploration and search for new deposits; secondly, the carbon intensity of the economy will be reduced and CO₂ emissions will be reduced.

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