TECHNICAL EVALUATION OF PROCESSES OF CHEMICAL TRANSFORMATION OF THE GAS METHANE IN PRODUCTS OF ADDED VALUE

EVALUACION TECNICA DE LOS PROCESOS DE TRANSFORMACION QUIMICA DE GAS METANO EN PRODUCTOS CON VALOR AGREGADO

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Abstract: The different potential sources of methane to be transformed into value commercial products are identified. The Technologies as steam reforming, selective oxidation, membrane reforming and thermal plasma are described. An analysis of the possibility of conversion of methane from anaerobic reactors and sanitary landfills into liquid hydrocarbon is done.

Keywords: Conversion of Methane, Steam Reforming, Syngas, Selective Oxidation, Hydrogen Production, Olefins, anaerobic reactor, Gas to Liquids, Fisher Tropsch process.

1. INTRODUCCIÓN

Methane (CH_4) is a colourless, odourless gas with a wide distribution in nature. It is considered a Greenhouse gas which traps over 21 times more heat per molecule than carbon dioxide [The Kyoto Protocol, 1997; ADEME, 2000, Kruger, 2000]. However methane also could be the beginning point of a thermo-chemical development, by means of the transference and implementation of clean development methodologies (CDM).

The aim of this work is to analyze different chemical routes for conversion of methane from diverse sources as sanitary fillings, anaerobic reactors and natural gas fields into products of greater added value. The technology Gas-To-Liquid (GTL) [Hill C., 1998], based on Fischer-Tropsch process [Meier R. et.al., 1998], developed in 1923 by Franz Fischer and Hans Tropsch. In this process a natural gas mixture (pulverized coal) is converted in gas of synthesis or syngas (CO_2/H_2), by partial oxidation with oxygen to 95%. In the

process, the syngas is passed over a metallic catalyst, like iron or cobalt, to produce a liquid mixture that contains molecules of long chain like kerosene and waxes. From a distillation process this mixture is refined to obtain clean fuels like gasoline or diesel engine. The advantage of the process of FTP is that the produced fuels are free of sulfur, heavy or aromatic metals found in conventional crude petroleum [Meier R. et.al., 1998].

Table 1 shows some of the most important projects on GTL developed by Petrochemical industries like, Shell, Exxon-Mobil, Mossgas, Sasol, BP-Amoco/Arco, Chevron, Texaco, Phillips, Conoco, Statoil, BG, Marathon, Murphy, RepsolYPF, Methanex among others. [Corzine R, 1997]. Between the important projects in execution the Sasol multinational in South Africa, with an investment of 1160 million dollars will produce 34.000 barrels/day (24.000 bbl of Diesel engine, 9,000 bbl of gasoline and 1.000 bbl liquefied gas). [Davies P., 2004].

Table 1: GTL Proyects in the world

Country	Calculated production	Operator	Status
Bolivia	10.000 bbl/día	Rentech	Announced
Nigeria	34.000 bbl/día	CNC&NNPC	Announced
Sudafrica	8.000 bbl/día	SASOLBURG - CTL	Operation status
Sudafrica	47.000 bbl/día	PETROSA	Operation status
Sudafrica	160.000 bbl/día	Sasol	Operation status
Saudi Arabia	140.000 bbl/día	Shell	Announced
Saudi Arabia	160.000 bbl/día	Conoco Phillips	Announced
Saudi Arabia	34.000 bbl/día	Sasol & Qatar Petroleum	Construction status
Saudi Arabia	66.000 bbl/día	Sasol Chevron & Qatar Petroleum	Announced
Saudi Arabia	130.000 bbl/día	Sasol Chevrom	Announced
Saudi Arabia	99.000 bbl/día	Syntroleum Marathom	Announced
Indonesia	16.000 bbl/día	Rentech	Announced
Indonesia	12.500 bbl/día	Shell	Operation status
Rusia	13.000 bbl/día	Syntroleum & Yakutgazprom	Announced

The FTP is formed by two stages: endothermic and exothermic. The investigation of GTL is centred in the development of coupled reactors in series that allow a greater efficiency in the conversion of gas to a smaller cost.

2. GAS SOURCES OF METHANE

Different sources of methane production are available: natural gas fields, sanitary fillings, anaerobic reactors.

2.1 Natural gas fields

The methane process of chemical transform has two routes: the use of gas like fuel or a chemical process of the gas to products of greater added value. The first one implies the development of an expensive infrastructure, with the environmental permissions. Also for its viability it requires sufficiently great and stable markets.

Latin America has important natural gas reserves that could be used in GTL processes. Figure 1 show the distribution of natural field gas in Latin America where Venezuela has the 49.12%. Bolivia plans the construction of a plant with capacity of production of 10,000 bbl/día of diesel engine with the GTL process [Inchaueste C., 2003]. On table 2 it is showed the gas natural fields in Colombia. [ECOPETROL, 2004].

With an investment of 500 million dollars a GTL plant could be constructed to produce Diesel engine, Gasoline and gas liquefied with capacity between 10,000 and 15,000 bbl/día, [Pinto N., 2004], in agreement with the reserves marketable natural gas of 4040 Giga cubical feet and with reserves of non-marketable natural gas of 2648 Giga cubical feet [ECOPETROL, 2003]
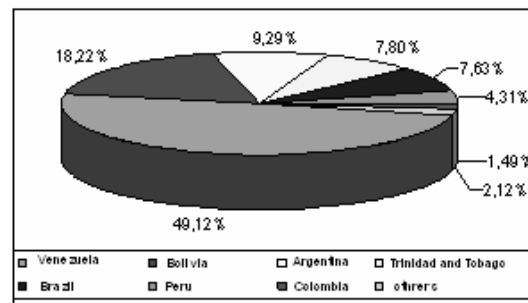

*Fig. 1. Latin America Gas reserves [Ecopetrol]*

Table 2: Main Gas fields in Colombia

Fields	Composition	Location	Calorific power
Ballen	CH_4=98, N_2=1.3,C_2H_6=0.249, CO_2=0.242	La guajira	996.7 Btu/ft^3
Chuchupa	CH_4=97.99, N_2=1.4,C_2H_6=0.266, CO_2=0.240	La guajira	997.3 Btu/ft^3
Guepaje	CH_4=96.74, N_2=2.3,C_2H_6=0.589, CO_2=0.047	Magdalena	996.2 Btu/ft^3
Cusiana	CH_4=78.8, C_2H_6=10, C_3H_8=3,93, CO_2=5.1	Llanos orientales	1124.6 Btu/ft^3
Apiay	CH_4=82.9, C_2H_6=12.44, C_3H_8=2.19 CO_2=0.242	Llanos orientales	1107.5 Btu/ft^3

Source: Betancourt, F., 2000; ECOPETROL, 2003

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2.2 Sanitary fillings

Sanitary fillings are sites for final disposition of organic waste so it concentrates the environmental impact decomposition due to leached liquids and gases with the negative effects on environment and public health [Greenpeace, 2004]. The stoichiometric equation for the fermentation of the organic matter is [Kenealy W. et.al., 1981; Turzo G. et.al., 1984; Yougfu, et.al., 1989]:

$$C_nH_aO_b + (n - a/4 - b/2)\ H_2O = (n/2 - a/8 + b/4)\ CO_2 + (n/2 + a/8 - 4)\ CH_4 \qquad (1)$$
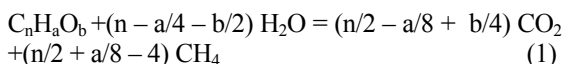
Where a, b and n are stoichiometric coefficient.

The amount of gases produced in sanitary fillings depends on variables related to the content of matter, humidity, etc. The composition of gases coming from the sanitary fillings is methane (55% vol), and carbon dioxide (45% vol). [Röben E., 2002] However, other toxic substances like, pesticides or compounds volatile organic persistent (CVOP's < 1%), generally, chlorinated, such as dioxins and furanos can be found. [Environmental Research Foundation, 1998]. The Environment Protection Agency (EPA) suggests a gas production in the rank of 63.7 m^3 to 81.6 m^3 by ton of sweepings. [Valdés S., 2004].

2.3 Anaerobic reactors

The use of microbes (methanogenics bacteria) in the absence of oxygen for the stabilization of organic material by conversion to methane, carbon dioxide, new biomass and inorganic products is the basic of a new bioindustry. The biogas produced contains between 50 and 70% of methane, and between 30 and 50% of carbon dioxide. Other gases as sulphur hydride and ammonia must be removed from biogas for their later use. [Ostrem K, 2004]. At least four groups of microbes have been isolated in anaerobic digesters: hydrolytic, fermentative, acetogenics, homoacetogenics and methanogenics bacteria [Marchaim O., 1992].

3. PROCESSES OF TRANSFORMATION OF METHANE

Thermochemical technologies of conversion of methane are classified in two routes: direct and indirect [Choudhary T. V. et.al., 2003, Fagundes, et.al., 2002] (Figure 2).

The direct route is based on the transformation of the methane by thermal and oxidative processes from which it is possible to produced olefins and gasoline. By the indirect route a syngas is obtained (H_2/CO), which by other processes is transformed into a great variety of chemical agents, as: gasoline, alcohol and paraffin. [Rahmim I. I., 2003]
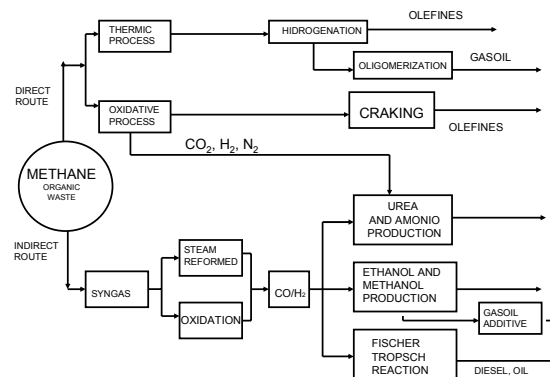

*Fig. 2. Processes of conversion of methane
[Rahmim I. I., 2003].*

3.1 Direct Route

Liquid products like alcohol (mainly methanol), olefins (ethylene and acetylene) and aromatic compounds (benzene, toluene and naphthalene) can be obtained. [Fagundes , et.al., 2002]. Low production and non selective processes are some of the problems of direct route. The actual investigation is focused on: improve of catalysts agents, identification of the mechanisms of reaction and development of equipment to increase the productivity of the process. [Martín G., 2001]. Even several processes of conversion have been developed, they has not been commercialized, because they are not economically attractive [www.chemlink.com.au/gtl.htm].
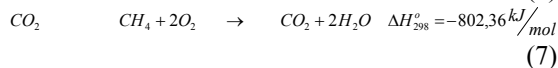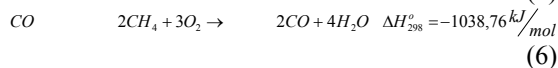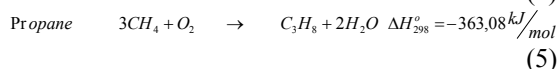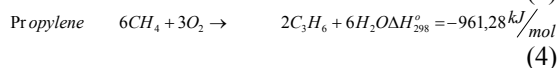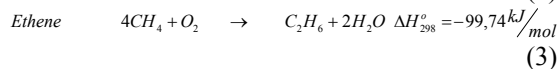
Synthesis of olefins and gasoline

The olefins might be made by means of a coupled oxidative process or by a thermal process. In the first process, methane is transformed into ethylene and propylene, products of great importance because they are used for polymer production. This process is carried out at low pressures (from atmospheric pressure to 5 atm), and at temperature of 750-900 °C [Josten J., 1998]. In addition, collateral reactions of free radical produce carbon monoxides (CO and CO_2) [Leveles L., 2002]. In the second stage, by craking process, ethane is transformed to ethylene and small amounts of C_3 (propane, propylene), C_4 (isopropane, butane).

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[Josten L., 1998]. In the oxidative reaction of methane, a replacement reaction of lithium by magnesium is used. [Ito, T. et.al., 1985]. Important details of the transformation of the methane are the conversion to C_2. In this process if the conversion is increased, it produces a fall in the selectivity of the product [Josten L.A.J, 1998]. On table 3 it shows some of products obtained form the methane conversion with a a selectivity of C_{2+} of 80-85%, [Geem, P. C., 1992].

Table 3: Composition of products of the conversion of methane.

Product	Composition [% mol]
Ethylene	50
Ethane	30
Propylene	1.7
Propane	3.7
CO	5
CO_2	10

The kinetic of the coupled reaction of methane has been described by mixed homogenous and heterogeneous models [Shi C., et.al., 2002; Sinev, M., et.al., 1995; Mims C., et.al, 1994]. The models include the heterogeneous formation of radicals and collateral. The following simplified reactions represent the process: [Ferstl J. et.al., 1994]:

$$Ethylene \quad 2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O \quad \Delta H^o_{298} = -281,78 \frac{kJ}{mol} \quad (2)$$

$$Ethene \quad 4CH_4 + O_2 \rightarrow C_2H_6 + 2H_2O \quad \Delta H^o_{298} = -99,74 \frac{kJ}{mol} \quad (3)$$

$$Propylene \quad 6CH_4 + 3O_2 \rightarrow 2C_3H_6 + 6H_2O \Delta H^o_{298} = -961,28 \frac{kJ}{mol} \quad (4)$$

$$Propane \quad 3CH_4 + O_2 \rightarrow C_3H_8 + 2H_2O \quad \Delta H^o_{298} = -363,08 \frac{kJ}{mol} \quad (5)$$

$$CO \quad 2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O \quad \Delta H^o_{298} = -1038,76 \frac{kJ}{mol} \quad (6)$$

$$CO_2 \quad CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \Delta H^o_{298} = -802,36 \frac{kJ}{mol} \quad (7)$$
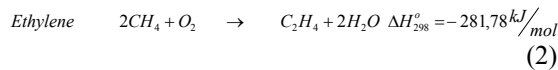
ΔH^O_{298}, values calculated from Atkins, 1998.

These reactions can be used to calculate mass balance: methane, oxygen and steam reformed [Josten L.A.J, 1998]. The coupled oxidative reactions offer a potential route to the direct conversion of light alkanes (C_1 - C_4) to products of greater value. [Kings S., et.al., 1993]. In the thermal process, the acetylene is used for liquid hydrocarbon and olefins production.

This process by two steps: first, methane goes to acetylene by heat treatment in a plasma reactor. In the second step, acetylene reacts with hydrogen to produce liquid fuels. [Anderson R. P. ET to, 2002] The direct route of methane conversion allows the production of olefins. However, this process falls in the selectivity of the products.

3.2 Indirect route

By means of SFT synthetic diesel and gasoline can be obtained [Choudhary T. et.al., 2003, Korobitsyn M.A. et.al., 2000]. Within the technologies there are:

• Reformed with steam
• Selective Oxidation
• Reformed with CO_2.

All the processes of syngas production is based on one or more combination of these technologies. An alternative technology is reformed with thermal plasma [Bromberg L., et.al., 1999; Bromberg L. et.al., 2000; Deminsky M., et.al., 2002]. This technology is related with the production of H_2 as a clean combustible.

Reformed with water steam

The reformed of methane with water steam is at the moment the main route for the conversion of syngas. The reaction is highly endothermic and it is produced on a nickel catalyst at high temperatures and at low pressures [Korobitsyn M.A. et.al., 2000]:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H^o_R = +206 \frac{kJ}{mol} \quad (8)$$
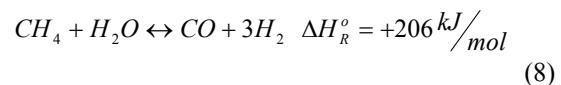
Gas burners inside the reactor are used to provide the energy of the reformed reaction [Stitt E. et.al, 2000]. The catalytic reformed process depends on the products to continue. [Stitt E. et.al., 2000; Lopez Ortiz T. et.al., 2001; Mertins F.H.B., 2005]. A second reformer reactor is not necessary in the case of methanol production or for SFT. The conventional catalyst contains between 10 and 33 % (w/w) of NiO on a mineral support (alumina, cement or magnesite) [Stitt E. et.al., 2000; Lopez O. et.al., 2001; Mertins F., 2005]. In addition the shift reaction occurs between the CO and steam which produces H_2 [Stitt, et.al., 2000; Lopez O. et.al., 2001; Tijmensen M. JA, 2000; Ogden J., 2001; Mertins F., 2005].

Reformed in simple stage

The reformed process depends on temperature of the reformed reactor at 850 ºC and on pressure about 15 atm [Lopez O., et.al., 2001]. For Tijmensen the operation temperature of the shift reactor shift must be of 330 ºC with pressures between 15 and 25 bars. At this condition, the composition of syngas will depend on the relation steam/hydrocarbon in the feeding. The syngas will have a relation 3:1 (H_2/CO) [Tijmensen M. JA, 2000]. This process has numerous disadvantages: [Stitt E., et.al., 2000]:
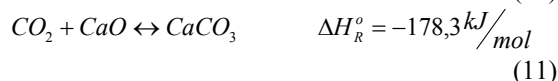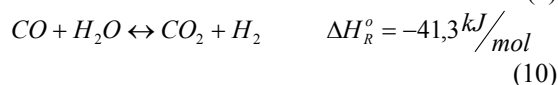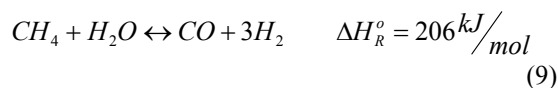• A high investment.
• The starting and shutdowns of the process are slow and require manual operations.
• The composition of the syngas is richer in hydrogen than the ideal for a synthesis of methanol or SFT.

From the traditional reformed process a series of modifications has been made:
• Modified reformed in simple stage.
• Autothermic Reformed
• Combined Reformed.
• Reformed by membranes.
• Reformed by plasma.

Modified Reformed in simple stage

In this process, the reactions of reformed, shift and of CO_2 removal are combined in a single container. [Adris et.al., 1996] The reactions at standard conditions are:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H_R^o = 206 \frac{kJ}{mol}$$
(9)

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_R^o = -41,3 \frac{kJ}{mol}$$
(10)

$$CO_2 + CaO \leftrightarrow CaCO_3 \qquad \Delta H_R^o = -178,3 \frac{kJ}{mol}$$
(11)

The natural gas and steam fed a reactor with the reformed catalyst and CaO for the CO_2 removal. The heat releases by the shift reaction is used by the reformed reaction. [Lopez O., et.al., 2001] The excess of CO_2 allows that the reformed reaction and the shift reaction take until the end. In this case hydrogen (95 %) is produced. To improved the purity of H_2, it will be necessary a later process to reduce the CO concentration [Lopez o. et.al., 2001]. This process is not the best to use gas from biological processes, because it contains 45% of CO_2, which in this process is eliminated with the use of CaO as $CaCO_3$, with a lower CO production.

Autothermic Reformed

This process combines steam with a partial oxidation reaction. Methane is partially oxidized to produce CO_2 and H_2O. The excess of heat produced affects positively the reformed catalytic process of the remaining reacts [Ogden Joan M, 2001]. The pure oxygen required for the reformed process might be supply from a cryogenic air unit. However it will increase the cost of the project [Dyer P., et.al., 2001; Higman C., 1990]. Nitrogen oxides might be formed if air is used. The conditions of operation of this process are: temperature of 900 ºC and pressure of 70 bars [Tijmensen M., 2000].

A natural gas ($CH_4 = 90\%$, $C_2H_6 = 6\%$, $C_3H_8 = 3\%$, $C_4H_{10} = 1\%$) requires a initial temperature of 550 ºC and a final temperature of 1050 ºC with a steam fraction of 0.6. The syngas produced will have a relation of 2.19 (H_2/CO). The CO_2 must be recycled to the ATR to increase the production of syngas to a proportion of 2,0 (H_2:CO) [Abbott P., et.al., 2002]. The catalyst agents are one of the most important variables. Transition metals like Pt, Rh and Ni, mixed with base metal oxides has been used. [Mawdsley J. et.al., 2005] The deposition of coke is the cause of catalyst agent deactivation.

Combined Reformed

In this process a net heat generation is made by a "Secondary" autothermic reformer. The exit gas is fed again to the reformer ("Gas Heated Reformer" or GHR) with the steam on a conventional nickel catalyst [Abbott P., et.al., 2002]. The primary reformer is replaced by a reactor of multiple heat interchange tubes. This process was developed by the ICI at the end of 80´s. [Armitage P, et.al., 1992] This technology has been applied successfully in the large-scale production of ammonia and for the production of methanol using oxygen as a second reformer [Farnell P., 1995; Vang C., et.al., 2001]. The technology reduces the costs of energy and the requirement of oxygen in a 10% and 25% by fuel barrel. Also the total CO_2 emissions are reduced in a 45% [Abbott P., et.al., 2002].
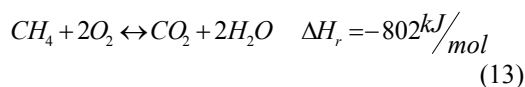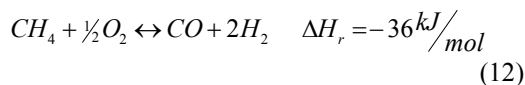
Reformed by membranes

There has been a considerable effort in operating the capacity of separation of membranes, altogether with the reformed reaction [Stitt E., et.al,, 2000; Dyer P., et.al., 2000; Dyer P., et.al., 2001]. There are two kinds of membranes:

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Oxygen addition: A mixed oxide membrane is used to separate the oxygen of the air with the purpose of feeding this oxygen within the current on gas. The transport mechanism is in fact an electrical device that requires temperatures in the order of 700 - 800 ºC to reach practical speeds of transport. Oxygen promotes a reaction of partial oxidation on the surface of the membrane with a catalyst agent. [Sammells T., 1999; Dyer P., et.al., 2000; Dyer P. et.al., 2001].

Hydrogen removal: A Palladium membrane is used to remove hydrogen from the reformed reaction [Sogge J., et.al., 1997; Dyer P., et.al., 2000; Dyer P., et.al,, 2001]. Due to the limitation of obtaining a palladium membrane with sufficient integrity and flow capacity, this technique will remain as a scientific curiosity

Oxidación selectiva (POX)

The process can be proposed by next reactions [Stitt E., et.al., 2000; Abbott P., et.al., 2002; Deutschmann, O., et.al., 2003]:

$$CH_4 + \tfrac{1}{2}O_2 \leftrightarrow CO + 2H_2 \quad \Delta H_r = -36 \, kJ/mol$$
(12)

$$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O \quad \Delta H_r = -802 \, kJ/mol$$
(13)

Even the reaction of partial oxidation is slightly exothermic, it can be more exothermic if the oxygen amount is limited so the oxidation can be a partial or total combustion [Stitt E., et.al., 2000] The relation H_2/CO of the reformed gas is near 2 and it has a favourable effect on the later processes of production of methanol and SFT [Stitt E., et.al., 2000; Deutschmann, O., et.al., 2003]. The process occurs in a reactor where the methane and oxygen preheated at a pressure of 40 bar are mixed in the burner. The oxidation reaction immediately happens in the combustion zone at a temperature of 1200 ºC without a catalyst agent and below 1000 ºC with a catalyst agent. This process produce a reduction of the oxygen fed. Under this conditions the destruction of the catalyst agent by thermal stress is produced [Korobitsyn M., 2000] and syngas produced is less rich in CO. [Higman C., 1990]

Even reactors of partial oxidation are smaller than the reactors of reformed steam. The efficiency is relatively high (70-80%), but in a global process the efficiency is smaller due to the absence of heat recovery [Pigneri, 2004]. The reformer of catalytic oxidation is affected by contamination and by the poison effect over the catalyst, as well as the sintering by thermal effect. [Kantak M., et. al., 2002]. The efficiency of the process of partial oxidation depends on: 1.- the conversion of the natural gas to hydrogen and carbon monoxide. 2.- The system capacity to recover the heat generated by the synthesis gas. This efficiency is increased using a system that turns the residual heat of syngas by means of the expansion in a gas turbine.

Reformed with CO_2

The use of greenhouse gases in the reformed reaction is one of the reason to develop a of technology to diminish the emissions to the atmosphere of these gases [Kraus M., et.al., 2001]. The use of CO_2 with a function similar to the steam with respect to the reform, in which the steam added in excess to inhibit the formation of the coke, besides diminish the cost additional use steam in excess for the reaction, is the basic idea. [Basini, L., et.al., 1998]. The proposed reformed reaction is [Korobitsyn M., et.al., 2000]:

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad \Delta H_r^o = +165 \, kJ/mol$$
(14)
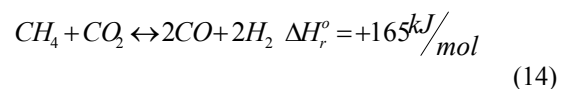
This reaction gives a low rate of H_2/CO, in relation with the steam use. [Korobitsyn M., et.al., 2000]. Prabhu, et.al.2000]. The use of membrane reactors improves the methane conversion in comparison with the reactor of fixed bed. [Prabhu, et.al., 1998]. Even Ni is one of the catalyst agent used in the reformed reaction with CO_2. [Hwang, et.al. 2000; Shamsi, et.al., 2002] This catalyst agent suffers a great damage by the carbon deposition on their surface, also the speed of formation of carbon is great that the speed of gasificación [Shamsi, et.al., 2002]. As a consequence a lower conversion of methane in the reaction is done. This is a reason to produce catalysts agents that allow the carbon deposition without been affected or inhibit this process in a high degree. The oxide of alkaline earth and metals with high basic character are not affected in their catalytic activity by the coke deposition. [Mansur J. et.al., 2002]

Reformed with Thermal Plasma

The plasma is a technology used for hydrogen production [Lu F., et.al., 2004] by an electrical arc in a reactor where the mixtures of reactants are introduced to form hydrogen, CO_2 and other

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products [Lynum S., et.al., 1998; Czernichowski, et.al., 1996]. The production of hydrogen is based on conditions of high temperature and degree of ionization. The favourable thermodynamic conditions accelerate the chemical reactions without a catalyst agent or thermal discharges to the endothermic processes [Bromberg L., et.al., 1999]. The main problem for the processes of hydrocarbon conversion arises from a kinetic limitation. With low kinetic speeds the use of expensive catalysts agents is necessary to improve the efficiency. [Deminsky M., et.al., 2002] Other problem comes from an operation restriction of cold start because the catalyst agent must be warm up before been used.

Because thermal plasma technology characterizes by temperatures between 3000 - 10000 ºC, It can be used to accelerate the kinetic one of the reformed reaction without catalyst agents. [Ogden, J., 2001] A methane conversion of 95 % has been obtained by the 14 Plasmatron of MJ/kg de H_2 [Bromberg L., et.al., 1999]. The thermal plasma is an attractive technology on a small scale for the generation of hydrogen, since it increases the efficiency in the reformed reaction without the catalysts agents so the operation cost is diminished. [Bromberg L., et.al., 1999]. In addition the reformed reaction with plasma can be associated to other process with steam and CO_2 [Huang, et.al., 2000], as well as with the pyrolysis of methane [Lu F., et.al., 2004].

4. CONCLUSIONS

Chemical transformation of the methane is affected by two factors: the consumption of energy and the degree of conversion. The optimal combination of these two variables can take to an efficient and profitable technology for the production of energy and chemical agents within the proposals of CDM. At the present time the types of processes for syngas production are reformed with steam and the selective oxidation or combinations of both. In the future lower cost processes for the conversion of methane can be developed with new emergent technologies as reformed with membranes and thermal plasma

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