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UTILIZATION OF RENEWABLE BIOGAS AND LADFILL GAS SOURCES FOR ETHANOL AND METHANOL SYNTHESIS

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ABSTRACT

An improved efficient catalytic method of ethanol synthesis is discussed from synthesis gas based on waste biogas and landfill gas resources. Wise utilization of waste biogas and landfill gases can be essential in the renewable area of energy and chemicals production. Improved practices for ethanol and methanol production that contribute to enhanced utilization of renewable resources are investigated in this article.

Ethanol can be produced via a direct catalytic one-step process from synthesis gas coming out from a conventional reactor or from a membrane type reformer.

Moreover, methanol synthesis from synthesis gas based on waste biogas and landfill gas resources is also discussed showing a significant potential.

The detailed flowsheet of the corresponding processes is presented to show the reactors pathway.

Keywords: ethanol/methanol production, biogas and landfill-gas conversion, catalytic membrane reformer, hydrogen and syn-gas utilization.

INTRODUCTION

It is important to be addressed that the production of biogas and landfill gas resources has been growing steadily for the last 25 years. There is a number of different sources today that produce these gases at global scale, especially as the earth population increases.

Today, most of the developed places in the world are looking for a relief from the increasing demand of energy and the large cost of oil and natural gas. This fact has heightened the focus in utilizing alternative and renewable energy sources. It is predicted that after 2050's, more than 50% of world energy demand will be produced from renewable energy resources. Energy security, economic development and protection of the today's world resources are the priorities of the national energy policy for many countries in the modern world. Utilization of waste-gases can be a partial solution to the requirements and expectations of the proposed renewable energy sources development.

In this paper, we report a new design and process for the capability of ethanol and methanol synthesis /production from renewable feedstocks such as biogas and landfill gas type sources.

Ethanol is a very important chemical component in the chemical industry. It can be used as antiseptic, antidote, anesthetic, medical solvent, for making several drugs in the pharmacology area, as an engine and rocket fuel, in a DEFC (direct ethanol fuel cell), in household heating and cooking, as a feedstock and chemical solvent, and in other uses as well.

Methanol is also a valuable chemical that can be used in several applications including its direct use as automobile fuel. Methanol, among others uses, can be converted into gasoline with the use of the Mobil zeolite process. Also, it can be used directly in a methanol fuel cell for direct electricity generation (DMFC).

Table 1 reports the composition of several related waste feedstocks for ethanol or methanol synthesis relating them with the composition of natural gas.

CO_2 is one of the main reactants for the methanol synthesis as it is described in the results section. Moreover, CH_4 and CO_2 are the reactants for the steam and CO_2 reforming reactions as well. H_2 is needed for both ethanol and methanol synthesis as well.

Further, H_2 can be optionally added in small quantities in the reformer inlet to prevent catalyst deactivation from carbon deposition. Table 1 reports the percentage composition of inlet waste/renewable gases for comparison purposes.

Thus, the chemical compositions of typical waste gases, coming from various sources, are shown in detail in the following Table 1 [10].

Table 1. Chemical Composition of Various Waste Gases [10]:

Components	Natural gas	Biowaste	Industrial waste	Landfill gas
CH_4	91 %	67 %	77 %	50 %
CO_2	0.5 %	33 %	23 %	43 %
N_2	0.6 %	0.2 %	Traces	5%
O_2	Traces	Traces	Traces	2 %
H_2	Traces	Traces	Traces	Traces
H_2S	Traces	<10 ppm	<10 ppm	300 ppm
CnHm	7.8 %	<10 ppm	<10 ppm	50 ppm

RESULTS AND DISCUSSION

Renewable sources of interest to this paper are the biogas and landfill gases. Two reaction methods are reported: Ethanol and methanol synthesis.

Syngas coming from the reforming of renewable sources such as biogas and landfill gases can be converted directly into ethanol or methanol in a catalytic synthesis reactor with significant yield and selectivity [3,4].

The syngas production outcome at various temperatures is presented in the Table 2 below [10]. It shows results from plant biomass such as wood ships. Biogas is coming from the treatment of biomass.

Table 2. Syngas production (kmol/ton of biomass) at various Temperatures (K) and Pressure of 24 atmospheres [10].

Temperature (K)	CH_4	H_2	CO_2	CO	H_2O
1000	8	12	20	12.5	12.5
1200	1	24	12	27.5	13
1400	0	24	9	31	14

Reforming of the above gases can take place catalytically usually in a fixed bed catalytic reactor or in a catalytic membrane reactor [1-4, 9, 11]. Mostly Ni, Cr, Rh, and Ru catalysts and their mixtures, are used in the reforming of biogas and landfill gases after their initial purification. Pd, Pt, Co and Fe catalysts have been also used but with lower yields in synthesis gas.

STEAM AND CO_2 REFORMING REACTIONS

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad \Delta H^0_{298} = 206.1\ kJ/mol \qquad (1)$$

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \qquad \Delta H^0_{298} = 247.3 kJ/mol \qquad (2)$$

$$H_2 + CO_2 \rightleftharpoons CO + H_2O \qquad \Delta H^0_{298} = 41.15\ kJ/mol \qquad (3)$$

CO and hydrogen are the direct products from the reforming reactions of such renewable gases as described in previous communications [1-4, 8-11].

The optional use of the membrane in the reforming reactor (membrane reformer or permreactor) provides more hydrogen at the exit streams so that the stoichiometry of the reactants in equations (1) and (2) is more easily satisfied.

A detailed flowsheet of the described processes is shown in Fig 1.

The flowsheet of the process consists of the inlet gas system, of the catalytic reactor (conventional reformer or membrane type reformer) and of the ethanol or methanol synthesis reactor where the corresponding discussed reactions take place.

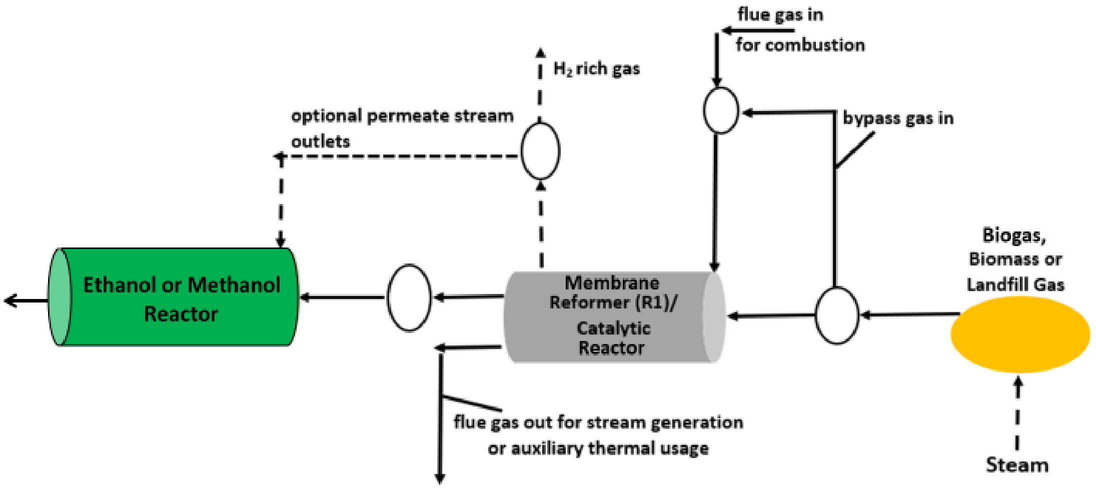

Figure 1. Flowsheet of the processes.

Figures 2 and 3 include both experimental and modeling results. The modeling results are produced based on the following mathematical model.

MATHEMATICAL MODEL

A theoretical model presented in the Figures 2 and 3 is described below:

The corresponding mathematical modeling of the methane-steam reformer for a steady-state fixed-bed catalytic reactor, including the species reaction terms in the mass balance equation, is as it is presented:

$$\frac{dX^A}{dz} = \left(\frac{\pi d_T^2}{4 n_{A_O}}\right) \rho_B R_A \qquad \text{(a)}$$

Species A can be any of the reactants and products of the reactions (1), (2) and (3).

With:

$$\begin{gathered} R_{CH_4} = -R_1 - R_2, \\ R_{CO_2} = -R_2 - R_3,\ R_{CO} = R_1 + 2R_2 + R_3, \\ R_{H_2} = 3R_1 + 2R_2 - R_3,\ R_{H_2O} = -R_1 + R_3, \end{gathered} \qquad \text{(b)}$$

where R_1, R_2 and R_3 are the heterogeneous reaction rates of the corresponding reactions given above.

In addition, the thermal balance in a nonisothermal reformer is given as follows:

$$\frac{dT_T}{dz} = \left(\frac{\pi d_T^2}{4}\right)\left(\frac{1}{m' c_p}\right) + \{\rho_B[(-\Delta H_r^1)R_1 + (-\Delta H_{\mathrm{r}}^2)R_2 + (-\Delta H_{\mathrm{r}}^3)R_3] - 4\left(\frac{U}{d_T}\right)(T_T - T_S)\} \tag{c}$$

Moreover, the reformer pressure balance which describes the pressure drop along the fixed bed of catalyst is given as follows:

$$\frac{-dP_T}{dz} = \frac{2f\rho_g u_s^2}{g_c d_p} \tag{d}$$

and the above equations are complemented by initial conditions as shown: at $z = 0$ (reactor/reformer inlet),

$$X^A = 0,\ T_T = T_o,\ P_T = P_{T_o} \tag{e}$$

A more specific analysis of the model, its parameters, and their variation is discussed in earlier communications [1,2,3].

The above system of governing equations (a) to (d) is integrated numerically as an initial value problem to provide the reactant conversions, product yields, reactor temperature, and pressure along the axial length and to obtain the axial profiles of these variables and their values at the reactor exit.

With the use of an inorganic permreactor/membrane reactor as the main catalytic processing unit to convert biogas/landfill gas feedstocks into synthesis gas, the above design equations are modified accordingly to include the permeation effects via the membrane of the different components.

Moreover, the following mathematical part has to be added at the right hand side of equation (a) to account for the permeation effects within the mass balance equation:

$$-\left(\frac{2\pi}{n_{A_o}^T}\right) P_{A,e}\left[\frac{p_A^T - p_A^S}{\ln{(r_1/r_2)}}\right] \tag{f}$$

wherein $P_{A,e}(\mathrm{gmol/s \cdot cm \cdot atm})$ is the effective permeability coefficient of species A via the catalytic or noncatalytic (blank) membrane.
Superscript T stands for the tubeside or reaction side of the membrane reactor, while S for the permeate side of it.

It is worthy to declare that in our experimental reaction studies we utilized mesoporous aluminum oxide membranes having a thin permselective layer (3-5 μm thickness, 50% porosity) with $40-50$Å pore diameter $[3]$. The membrane is a multilayer structure supported on an a-alumina support $(1.5-2.0$ mm thickness, $40-45\%$ porosity, and $10-15\mu$m pore diameter).

When a permreactor/membrane reactor is used, the corresponding mass, temperature, and pressure variation equations are written as well for the gas which permeates via the membrane wall material and flows in the permeate side (S) of the membrane reactor.

It is assumed that there are no reactions occurring in the permeate membrane side. An analysis of the model for the permreactor has been described as well in earlier communications [3].

By employing equations (a) to (f) within the modeling procedure, a complete reactor analysis is obtained for the two different reformer configurations. Solution of the equations is obtained numerically by using an initial value integration technique for ordinary differential equations with variable stepsize to ensure higher accuracy (implicit Adams-Moulton method) [1,2,3].

In our previous papers, we have described and analyzed the reaction, separation (i.e., permeation), and process (conversion, yield) characteristics of membrane based catalytic reactors and related processes for methane steam reforming, water-gas shift, and methane carbon dioxide reforming reactions including catalysis and membrane materials characteristics.

The main categories of reactors described were membrane reformers which were utilized as single permreactor [1,3], permreactor-separator in series or reactor-separator in series and permeactor-permeactor in series [3].

COMPARISON OF EXPERIMENTAL AND MODELING STUDIES

In Fig. 2 there are experimental and simulation/modeling results for the methane conversion from the catalytic plug flow reactor (PFR) of the reforming reactions (1) and (3) taking place together [3].

The conversion is increased as the reaction temperature increases as it is expected since it is an overall endothermic reaction. It also increases as the space time of the reactor increases.

The significance of this work, is also the fact that there is a satisfactory agreement between the modeling and experimental data [1-3].

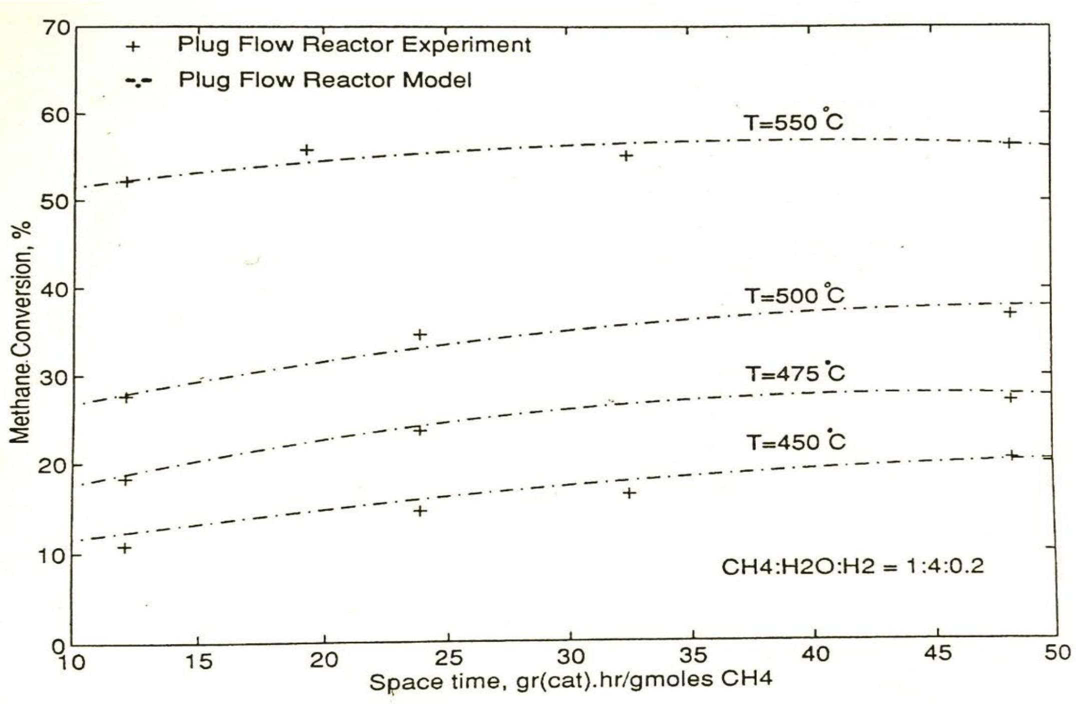

Figure 2. Methane Conversions vs Space times at various reaction Temperatures from both experimental and simulation/modeling data of a Plug Flow Catalytic Reactor.

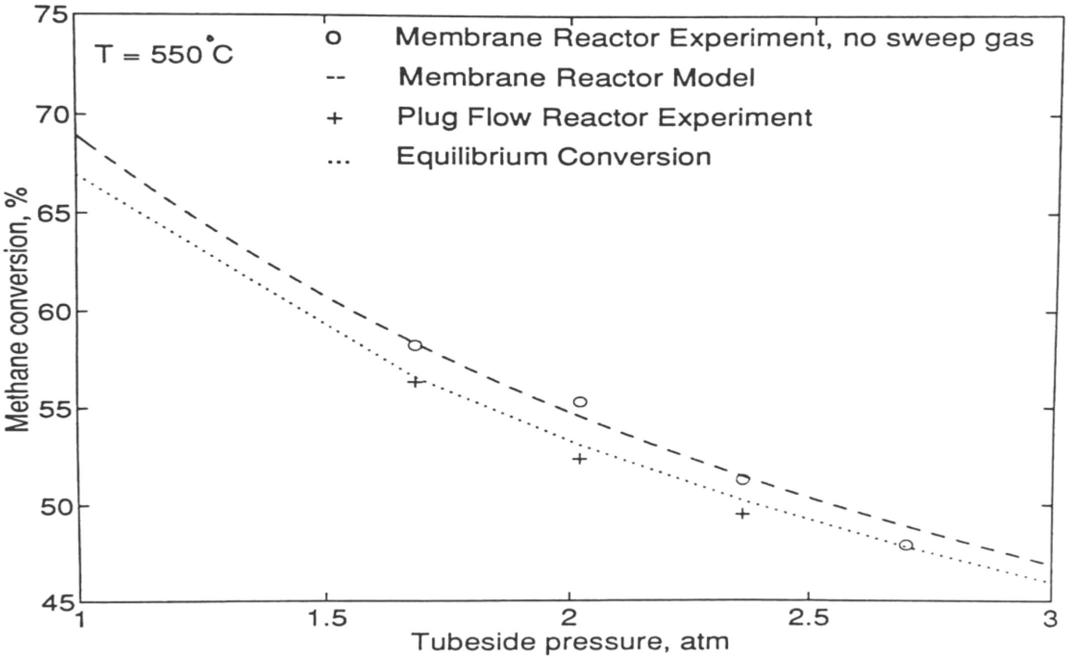

Figure 3. Methane Conversions vs various tubeside reaction pressures from both experimental and simulation/modeling data of a Plug Flow Catalytic Reactor and a Plug Flow Catalytic Membrane Reactor.

Moreover, methane conversions for the plug flow and membrane reactors at various rea tubeside reaction pressures of the reactors are shown in Fig. 3 for the same reactions as in Fig.2. The reaction temperature is fixed at 550 ^{o}C. Results from the modeling studies together with the corresponding calculated thermodynamic equilibrium conversions are included in the figure [3]. As it is expected, the conversion is decreased as the tubeside pressure increases because we have an overall volume expansion reaction.

The membrane reactor performs better than the conventional plug flow catalytic reactor and overcomes the equilibrium limited conversions. At all cases, the model agrees well with the experimental data [1-3].

Methane conversion is measured as follows:

(moles of methane in - moles of methane out) / moles of methane in (%).

The specific $CH_4:H_2O:H_2$ = 1:4:0.20 feed ratio, in the two figures, is defined as the ratio of the reactants in the reformer inlet, and used as an optimized one for best results.

H_2 is needed in the reformer inlet to avoid catalyst deactivation, and steam used as a main reactant in excess. The detailed description of the theoretical simulation model used in Figures 2 and 3 was presented above.

ETHANOL SYNTHESIS REACTION

The direct ethanol process from the CO and H_2 gas constituents is projected more economic and efficient than other competent methods of ethanol synthesis [3,5-7,12].

The direct exothermic synthesis reaction is given below in equation (4):

$$2CO + 4H_2 \rightleftharpoons C_2H_5OH + H_2O \qquad \Delta H^0_{500} = -28.4 \text{ kJ/mol} \qquad (4)$$

Ethanol synthesis and selectivity are shown at various temperatures at the Table 3 for catalytic reaction using catalyst of K^+–ZnO–ZrO_2 | H-MOR–DA–12MR | Pt–Sn/SiC system and are consistent with the literature [12].

Various catalysts and their mixtures can be used for ethanol synthesis such as Cu, Co, and Rh, Ru, Pd, Pt and Fe based metals as described in previous pertinent communications [3-7,12]. Depending on the catalyst used and the other details of the reaction, the conversion, yield, and selectivity to ethanol varies at different levels. The corresponding analysis is a subject of future study as well.

Ethanol selectivity is defined as follows:

(moles of ethanol produced / moles of all products) %.

During the ethanol synthesis reaction olefins and CO_2 are produced as byproducts as well.

Methane reforming reactions are favorable at higher temperatures since there are endothermic reactions. However, ethanol synthesis reaction is favorable at lower temperatures since it is an exothermic reaction. Therefore, operation at lower temperatures gives the best achievable results for ethanol synthesis with better energy consumption.

Beyond ethanol synthesis the valuable synthesis gas coming out of the reformer can be used in other usages such as a feed in high temperature solid oxide and molten carbonate fuel cells for electricity generation [1-4, 8, 9]. Work in this area is continuing within our research group.

Table 3. Conversion and Selectivity to Ethanol at various temperatures [12].

Temperature (^oC)	500	550	590	630	640
Conversion to Ethanol %	9.2	8.1	7.3	5.2	3.7
Ethanol Selectivity %	90	81	70	50	33

Syngas from the reformers can be also utilized to produce methanol as we have discussed at previous communications [3,4,8].

METHANOL SYNTHESIS REACTIONS

$$CO + 2H_2 \rightleftharpoons CH_3OH \qquad \Delta H^0_{298} = -128.2\ kJ/mol \qquad (5)$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \qquad \Delta H^0_{298} = -49.5\ kJ/mol \qquad (6)$$

The achieved conversions to methanol have been investigated and reported under different catalyst operating conditions and are presented in Table 4 below [13].

Table 4. Conversion to Methanol for various temperatures and catalysts [13].

Temperature at various catalysts	Commercial catalyst at 220 ^0C	Nanocatalyst at 220 ^0C	Mixed oxide catalyst at 240 ^0C

Conversions to Methanol	18.9%	22.6%	36.3%

Moreover, there is a potential study for ethanol synthesis from CO_2 and H_2 which can be of further research interest after a proper catalyst is found. The investigation of the proper catalyst is a demanding task and opens a complete new section for further study. This is an important reaction because it utilizes the waste CO_2 as the main reactant. Research in this area is continuing within our group. The reaction is as follows:

$$\mathbf{2CO_2 + 6H_2 \rightleftharpoons C_2H_5OH + 3H_2O} \qquad \mathbf{(7)}$$

CONCLUSIONS

In this communication, the direct production of ethanol and methanol from synthesis gas has been discussed using biogas and/or landfill gas sources.

A catalytic reformer and membrane reformer for syngas production are presented including experimental and modeling results that show satisfactory fitting at various temperatures, pressures and space times. Moreover, the membrane reformer seems to perform better than the conventional catalytic reformer.

The conversion to ethanol and selectivity are shown to indicate operation at lower temperatures with the highest outcome.

Methanol synthesis under different catalysts and temperatures has been also addressed. The discussed processes are shown in a detailed flowsheet.

Energy security, economic improvement, and environmental protection of the various resources have to be the priorities for every country in the modern society.

In conclusion, turning waste renewable gases into chemicals (such as ethanol and/or methanol) is not only a viable solution with important potential to reduce the dependence on fossil fuels, but also a wise and efficient way to produce valuable decentralized energy with a smaller carbon footprint.

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