Co-Al and Mn-Fe Catalytic Steam Reforming of CH$_3$OH to H$_2$.

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Abstract: Catalytic production of hydrogen by steam methanol reforming (SMR) is an attractive option for specific applications in fuel cells, decentralized generation of H$_2$ or localized boosting of the energy content of digestion gas. Supported metal catalysts integrate the endothermic methanol steam reforming with the exothermic Boudouard reaction. The paper reviews the fundamentals of SMR, develops 2 self-made, cheap and efficient catalysts, and demonstrates that high H$_2$ yields with low CO and CO$_2$ by-product formation. Present methanol reformers are mostly of the packed bed type which suffer from problems of temperature gradients within the catalyst bed and a slow response during start up and transients. In using a vibrated fluidized bed of the micron-size catalysts, a uniform bed temperature is achieved. More than 600 L/hr of hydrogen can be generated at methanol conversions in excess of 95%. A too high space velocity in the catalytic bed significantly reduces the methanol conversion, however without affecting the H$_2$ yields. The assessed systems clearly merit pilot plant research.

Keywords: methanol, steam reforming, catalysts, vibrated fluidized bed reactor, solar energy, yields, scale-up

1. Introduction

1.1. Hydrogen to decarbonize the energy sector

Although H$_2$ is key to produce value-added products, nearly all routes generating hydrogen from fossil hydrocarbons will lead to CO$_2$ and GHG emissions. There are 3 types of H$_2$ based on their source of production [1]: ‘green H$_2$’ (non-fossil process, very low carbon emission), ‘grey H$_2$’ (hydrocarbon sources with carbon emission) and ‘blue H$_2$’ (hydrocarbon sources with captured or utilized carbon emissions). The hydrogen production technology using the fossil-fuel based feedstock can be divided into the steam reforming (SR), the partial oxidation (POX), and the auto-thermal reforming (ATR) processes, respectively [2]. Non fossil fuel feedstock processes involve fermentation [3], biomass gasification/pyrolysis [4], electrolysis [4], among others. Table 1 compares the processes from previous literature data [1,2,4].
### Table 1. Comparison of current reforming technologies

| Technology                | Cost [$/kg] | Advantages                                                                 | Drawbacks                                      |
|---------------------------|-------------|-----------------------------------------------------------------------------|------------------------------------------------|
| Steam reforming           | 2.27        | Well established technology; no O₂ required; lowest process temperature, and highest H₂/CO ratio | High production of CO, CO₂                     |
| Partial oxidation         | 1.48        | Decreased desulfurization required, no catalyst required, low methane slip.  | Low H₂/CO ratio, very high processing T, soot formation |
| Auto-thermal reforming    | 1.48        | Low process temperature and low methane slip.                               | Requires air or O₂, CO₂-byproduct              |
| Bio photolysis            | 2.13        | CO₂ is consumed, O₂-byproduct, mild operation conditions                   | Low H₂ yields, sunlight needed, large reactor required, O₂ sensitivity |
| Gasification/Pyrolysis    | 1.59-2.05   | Abundant and cheap biomass feedstock and nearly CO₂-neutral                | Fluctuating H₂ amount, tar formation           |
| Thermolysis               | 7.98–8.40   | Clean and sustainable, O₂-byproduct, excessive feedstock                    | Elements toxicity, high capital costs, corrosion problems |
| Photolysis                | 8–10        | O₂-byproduct, abundant feedstock, no emission                              | Low efficiency, requires sunlight              |
| Electrolysis              | 10.30       | Zero emission, existing infrastructure, O₂-byproduct                       | Currently using fossil-fuel based electricity  |
| (Photo or Dark) fermentation | 2.57-2.83  | Easily combined with wastewater treatment, CO₂-neutral                     | Low H₂ yield, huge reactor volume              |

### 1.2. Properties of hydrogen and Barriers to fuel-H₂

H₂ is an efficient and sustainable clean energy carrier, used to substitute the fossil fuels due to its high energy content [5]. A unit weight of hydrogen can generate nearly 33 kWh energy [6]. Although nearly absent in nature, it can be produced by different techniques, as highlighted in Table 1.

A major hurdle in the hydrogen economy lies in its transport and storage due to its low volumetric energy density. Liquefied or pressurized hydrogen can enhance the energy density, but at a cost of added energy consumption [7]. An additional problem is the H₂ corrosiveness (steel embrittlement or liner attack) during storage. Hydrogen moreover has one of the widest explosive/ignition ranges with air. Safety measures are hence of primary importance [8].

Despite the challenges described above, the use of H₂ has significant advantages in decarbonizing the industrial (cement, limestone, glass, steel) and energy production industries [9]. The most promising are energy-efficiency improvements, the use of hydrogen made with zero-carbon electricity as a feedstock or fuel, the use of biomass as a feedstock or fuel, and the end-of-pipe carbon capture and storage (CCS) or usage (CCU). The optimum mix of decarbonization options will vary from facility to facility, even within the same sector, because local factors determine which ones are most practical or economical.
1.3. The limited but important applications of methanol steam reforming

Since the objective of producing “green” hydrogen is of paramount importance, it would be misleading to propose the hydrogen production by steam reforming of methanol as a top priority. Methanol is mostly fossil-fuel based, and its partial conversion to H₂ will not meet the “green” objectives since the methanol production itself is H₂-based. Contrary to other H₂-sources, such as ethanol, NH₃ or even CH₄ as produced by anaerobic digestion, the production of bio-methanol is still at its lab- or pilot scale development shape, as illustrated in table 2.

Table 2. Bio-methanol technologies and their application

| Technology Name/owner | Feedstock | Project | Project phase | Product | Plant capacity |
|-----------------------|-----------|---------|---------------|---------|---------------|
| SES Gasification Technology (U-Gas) | Biomass/ MSW | Trans World Energy, Florida (US) | Front-end engineering: done, start-up Q2 2023 | Methanol | 875 kt/y |
| NextChem Technology | MSW | ENI Refinery, Livorno, Italian (IT) (NextChem) | Basic engineering ready Q3 2020 | Methanol | 115 kt/y |
| | MSW/Waste wood | LowLands Methanol (NL) (2020) | Start-up early 2023 | Methanol | 120 kt/y |
| HTW/Thyssenkrupp | Biomass | V.rmlandsmetanol (SE) (2017) | Planning | Methanol | 100 kt/y |
| Enerkem (Enerkem, 2020a) | MSW | Rotterdam (NL) | Engineering | Methanol | 215 kt/y |
| | MSW | Saragossa (SP) | Engineering | Methanol | 215 kt/y |
| Steam reforming | Natural gas/biomethane | BASF, Ludwigshafen (DE) | Operational | Methanol | 72 kt/y (2018) |
| | | OCI/BioMCN Groningen (NL) | Operational | Methanol | 60 kt/y (2017) |
| | | OCI Beaumont Texas (US) | Operational | Methanol | 1 075 kt/y (2020)* |
| Andritz | By-product from wood pulping | S.dra Mill, M.nster.s (SE) | Operational | Bio-methanol | 5.25 kt/y |
| Not known | | Alberta Pacific (CA) | Operational | Bio-methanol | 3 kt/y |

* Bio-methanol share not given

Since the production is currently limited, there are limited data about production costs, although at the first information reported confirms that the biomass and efficiency of the processes will be determining the - yet undefined - viability.

There are however immediate applications of smaller-scale steam-methanol reforming due to the facility of transporting and storing methanol rather than H₂. Such applications can be the (i) the on-board (car) production of H₂ to feed fuel cells, with a significant advantage that the on-board methanol tank will weigh about 15% of the H₂ tank; (ii) the decentralized H₂ production for industrial applications, such as vegetable oil hydrogenation, thus avoiding expensive and dangerous H₂ transport or distribution networks; (iii) the H₂ generation is boost the energy content of digestion gas prior to its use in gas engines, thus also decarbonizing this CHP application. The current market for fuel cell application is very competitive with high demands and expectations to compete with internal combustion engines. Although these cars can travel between 400-600 km and generate 100kW, there is still a long way to go to achieve the consumers’ satisfaction since safety, reliability, travel distances and refueling remain issues of concern [10].
1.4. Objectives of the research
The present paper will discuss the steam reforming of methanol to hydrogen at temperatures below 350 °C and using novel self-made Al₂O₃-supported Co and MnFe₂O₄ catalyst. The dependence of the catalytic activity and selectivity on the reaction temperature, the H₂O/CH₃OH molar ratio and the contact time were studied. The stability of the catalyst in view of potential coking was moreover investigated.

2. Steam reforming of methanol
2.1. Review of the production methods and reaction pathways
There has recently been extensive research on the methanol steam reforming process. MSR is demonstrated to be a proper way to provide hydrogen with high yield for the fuel cell applications, while the CO selectivity is very low. The overall reaction network of methanol steam reforming process can be described as follows:

\[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + 3\text{H}_2 \quad \Delta H = 49.7 \text{ kJ/mol (1)} \]

\[ \text{CH}_3\text{OH} \rightleftharpoons \text{CO} + 2\text{H}_2 \quad \Delta H = 90.2 \text{ kJ/mol (2)} \]

\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \quad \Delta H = -41.2 \text{ kJ/mol (3)} \]

The general operating conditions of this process are an operation at atmospheric pressure, between 250 and 300 °C, and a methanol/water molar ratio between 1 and 1.5. The overall reaction (1) comprises the combination of methanol decomposition (2) and water-gas shift (3) reactions. The main products of the process are hydrogen and carbon dioxide, although trace amounts of CO are produced by the reverse water-gas shift reaction at high temperature. Peppley et. al reported that the methanol decomposition reaction rate is much lower than that of the steam reforming reaction, and adding water to the feed decreases the temperature where methanol decomposition begins [11,12]. It is moreover demonstrated that the absence of steam in the feed leads to coke formation [13]. Another study showed that there is no CO formation at low contact times [14].

In spite of numerous investigations on MSR reaction process, the reaction mechanism is still a controversial issue due to the reaction complexity. Two reaction mechanisms, rather than methanol decomposition followed by water-gas shift reaction, have been postulated as follows:

(A) via methyl formate:

\[ 2\text{CH}_3\text{OH} \rightarrow \text{HCOOCH}_3 + 2\text{H}_2 \quad (4) \]

\[ \text{HCOOCH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{HCOOH} \quad (5) \]

\[ \text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2 \quad (6) \]

(B) via formaldehyde:

\[ \text{CH}_3\text{OH} \rightarrow \text{HCHO} + \text{H}_2 \quad (7) \]

\[ \text{HCHO} + \text{H}_2\text{O} \rightarrow \text{HCOOH} + \text{H}_2 \quad (8) \]

\[ \text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2 \quad (9) \]

To the extent of our knowledge, a detailed MSR mechanism study has not been done yet. Consequently, the controversy still remains on the real mechanism of this process.

2.2. Scientometric assessment of research developments
The conversion of methanol has been a research topic over the past decades, as illustrated as Figure 1 below.
Figure 1. Publication history with keywords: methanol, decomposition, hydrogen, steam reforming. 334 papers were found using WoS.

Although mostly Cu-based catalysts were investigated, other metals were additionally promoted, such as Ni and Zn, Fe and Mn, Co, among others. Pd, Pt, Au, Ru, Rh were also investigated but to a lesser extent due to the costs of the metals. The evolution of the research is illustrated in figure 2 with main research (the bigger circles) topics being the XRD of the catalysts, the reaction and dehydrogenation efficiency and the products being formed.

Figure 2. Interaction of different research topics.

The research topics shifted over the past decades, from 2006-2008: CuO, Cu$_2$O, fuel, double hydroxide; to 2010-2012: decomposition, ethanol steam, activation energy, gasification; and via 2013-2015: solar energy, methanol steam reforming; to 2015-2021: metal surface, side reaction, catalyst deactivation.
2.3. Thermodynamic equilibrium calculations

The conversion of methanol by thermo-catalytic reactions is governed by both reaction kinetics and reaction equilibrium. Prior to assessing the kinetics of the reactions, it is important to study the complex equilibria of the destruction reactions within the further applied temperature range of 150-350°C. These equilibria can be studied either by solving the simultaneous equilibrium expressions or by minimizing the total free energy.

The method of simultaneous equilibrium expressions requires the connected solution of two or more equations written in terms of the extents of reaction, each with separate equilibrium constant. The equations can be solved for equilibrium concentrations with a good non-linear algebraic equation solver, starting from initial estimates. Stoichiometric equations for reactions thought or known to occur are needed, but no more than one way to make each product should be taken into account. Of course, a given compound may appear in several equations, but only when all of these equations are necessary to introduce other products. This approach is presented by AspenPlus (version 10.2) and referred to as "REQUIL".

The total free energy for a reacting system reaches its minimum at equilibrium, and the corresponding product composition can be found by determining the combination of component characteristics that produces such a minimum. The following general equation applies for ideal gas systems:

\[
\frac{G}{RT} = \sum_{j=1}^{c} n_j \left( \frac{G_f^0 + \ln P + \ln \frac{n_j}{n_T}}{RT} \right)
\]

(10)

With \(R\): gas constant \((0.082506 \text{ m}^3 \text{ atm})/(\text{mol K})\),
\(T\): temperature (K),
\(G_f^0\): standard free energy of formation of component j at 1 atm and temperature T (kJ/mol),
\(P\): total pressure (atm),
\(n_j\): molar amount of component j (mol),
\(n_T\): total number of moles in mixture (mol),
\(c\): number of components in the system.

For non-ideal gases, the mole fraction of each component must be multiplied by the applicable fugacity coefficient.

In order to find the number of moles of each component at equilibrium, the values determined must yield a minimum in the value \(G/RT\), and simultaneously be constrained by the elemental balance requirement:

\[
\sum_{j=1}^{c} a_{ij} n_j - b_i = 0, \text{ for } i=1, \ldots, p
\]

(11)

where \(a_{ij}\) is the number of atoms of element i in component j,
\(b_i\) is the total number of atomic weights of element i in the system,
\(c\) is the number of components in the system,
\(p\) is the number of elements in the system.

Lagrange multipliers are introduced in this search for a minimum by adding a term to the free energy, thus obtaining a Lagrangian function:

\[
L = \sum_{j=1}^{c} n_j \left( \frac{G_f^0 + \ln P + \ln \frac{n_j}{n_T}}{RT} \right) - \sum_{j=1}^{p} \lambda_i \left( \sum_{j=1}^{c} a_{ij} n_j - b_i \right)
\]

(12)

Where \(\lambda_i\) is the Lagrangian multiplier.

The partial derivatives with respect to the compositions set to zero, provide the criteria for a constrained minimum of the function \(G/RT\):

\[
\frac{\partial L}{\partial n_j} = \frac{G_f^0}{RT} + \ln P + \ln \frac{n_j}{n_T} + 1 - \sum_{j=1}^{p} \lambda_i a_{ij} = 0, \text{ for } j=1, \ldots, c
\]

(13)

Various methods proceeding from this point have been described, all starting from estimates of the mole fraction. The derivatives are solved for these mole fractions and further manipulation yields \(n_T\). Additional equations are hence produced from which the Lagrange multiplier can be calculated and used for estimating new values of mole fractions at equilibrium for the next iteration step. As an alternative
to the Lagrangian multiplier technique, any non-linear programming procedure for constrained minimization can be used. The unique value of the method is that knowledge of the equilibrium constants of all chemical reactions that lead to products is not required, and that the solution method can proceed with arbitrary guesses of the equilibrium composition. This approach is used by the "RGIBBS" programme of AspenPlus (version 10.2). The equilibrium calculation of the reaction by the above method is illustrated in Figure 3.

![Figure 3. Equilibrium product distribution for steam reforming of methanol, at 1 bar and a 1:1 molar ratio of CH$_3$OH/H$_2$O.](image)

Clearly higher temperatures foster the (unwanted) CO production, whereas temperatures up to 525-550 °K maintain a high H$_2$ production.

3. Experimental investigations

3.1. Catalyst preparation

Co/Al$_2$O$_3$ catalysts: The catalysts were prepared by impregnating the support (Al$_2$O$_3$) with the solution of Co(NO$_3$)$_2$ to yield a 10% metal content. The impregnated powders were dried at 383 K for 2 h in a vacuum oven. Before each measurement the catalyst particles were calcined in N$_2$ atmosphere at 973 K with a heating rate of 20 K/min for 5 h.

MnFe$_2$O$_4$ catalysts: MnCO$_3$ (99%), Fe$_2$O$_3$ (97%), and Na$_2$CO$_3$ (99.5%) were used without further treatment. Na$_2$CO$_3$, Fe$_2$O$_3$, and MnCO$_3$ (molar ratio of 3:2:2) was mixed in Simoloyer CM01 mixer/mill after addition of ethanol (96%) under ambient condition. The mill is operated at 1000 rpm, 20°C for 40 min. The weight ratio of balls (5 mm diameter stainless steel) to powder is 6.

3.2. Experimental rigs and methods

Two experimental rigs were used in the study.
Firstly, isothermal conversions at a given \( \text{CH}_3\text{OH}/\text{H}_2\text{O} \) feed ration and set temperature were determined by macro-thermogravimetric analyzer (electrically-heated macro-TGA). The set-up is illustrated in Figure 4. The bottom section preheats the mixed methanol/water feed. The reaction starts above the distributor. The catalyst bed was between 0.12 and 0.15 m deep. The produced gas mixture was continuously monitored by gas chromatograph, whereas samples were also collected on activated carbon adsorption probes for subsequent GS-MS determination of specific compounds. A carrier flow of 40 +/- 2 mL/min of \( \text{N}_2 \) was used.

![Figure 4. Lab-scale set-up (electrical furnace)](image)

Secondly, solar \( \text{H}_2 \) reductions were carried out in the solar thermal furnace, depicted in Figures 5 and 6. The cavity of size \( 0.5 \times 0.5 \times 0.5 \text{ m}^3 \) has an irradiation orifice of 0.3 m diameter. The maximum heat load in the cavity can be ~ 20 kW. To maintain the reactor inside the cavity at the proposed temperature, the concentrating heliostat was partly de-focused. A vibrating fluidized bed was installed inside the cavity (Figure 5 and 6). The wall temperature of the vibrating reactor was 80 to 100 °C above the required catalyst bed temperature. The internal diameter of the vibrated fluidized bed reactor was 50 mm. Methanol and water were preheated by a coil heat exchanger also installed in the cavity. A multi-orifice distributor was used to ensure a uniform gas distribution in the fluidized bed reactor [10]. The operation conditions involved the use of an inert fluidizing gas (\( \text{N}_2 \)), a superficial bed velocity below 0.02 m/s, a vibration frequency and amplitude of 25 to 47.7 Hz and 0.6 mm, respectively. Reaction temperatures between 473 and 623 K were investigated. The pressure drop was checked in real time using a differential pressure transmitter (Rosemount Inc., USA) through pressure drop ports just above the distributor and at the top of the reactor. Nitrogen was used as fluidization gas at start-up (till the desired bed temperature was obtained) and at shut-down. Auto-fluidization was obtained by the released \( \text{H}_2, \text{CO}/\text{CO}_2 \), and excess water vapor once the decomposition had started.
4. Experimental results and discussions

4.1. MSR conversion

Results are presented in Figures 7 and 8.

![Catalytic decomposition of Methanol-water (1:3) mixture using Co-Al₂O₃ or MnFe₂O₄ catalyst. Results obtained in the electric furnace at the given temperatures](image-url)

**Figure 7.** Catalytic decomposition of Methanol-water (1:3) mixture using Co-Al₂O₃ or MnFe₂O₄ catalyst. Results obtained in the electric furnace at the given temperatures
Figure 8. Methanol-water (1:3 mixture) using the MnFe$_2$O$_4$ catalyst. Results obtained in the electric furnace at 300 °C

No coking of the catalyst was observed, and up to 10 repeat experiments or the same length of contacting time and t successive days yielded the same H$_2$ production rates. Average results of 3 repeat experiments were shown in the above results. The deviation between the repeat results and the averages were below 10%, accepted as fair in view of the lag time in the reactor piping.

4.2. Effect of the catalyst contact time

The results at a given concentration ratio of CH$_3$OH/H$_2$O (= 1.3) were repeated at different values of the hourly space velocity, being the ratio of the volumetric gas flow ate through the reactor, and the catalyst bed volume. Figure 9 illustrates the results, stressing that a gas hourly space velocity in excess of 50/hr significantly decreases the methanol conversion, however with an increased H$_2$ production yield (and less CO/CO$_2$ by-products)

Figure 9. Hydrogen production and methanol conversion at 275 °C as function of gas space velocity
5. Conclusions and recommendations

The research confirms that the catalytic production of hydrogen by steam methanol reforming (SMR) is attractive. Both $\text{Al}_2\text{O}_3$-supported Cobalt and Manganese ferrite are good catalysts at moderate temperatures. The solar thermal methanol reforming in a vibrating fluidized bed of the micron-size catalysts is proven successful and is very interesting for scale-up. At 250 to 300 °C and a surface velocity of about 50 hr$^{-1}$, the methanol conversion in nearly complete with a H2 yield of ~80 %., the remaining 20% being split between $\text{CO}_2$ and CO.

6. References

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