2012 International Conference on Clean and Green Energy
IPCBEE vol.27 (2012) © (2012) IACSIT Press, Singapore

Efficient Conversion of Natural Gas and Biomass into Fuel without External Input of Hydrogen

Nitish Mittal [1]

[1] Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur, India 208016

Abstract. One of the problems faced in the gasification of biomass is that it does not convert all the carbon atoms into carbon monoxide. Around half of them get converted to carbon dioxide. In order to improve yields of carbon monoxide, a stream of carbon dioxide and hydrogen is co-fed to favor reverse water –gas shift reaction. However, the requirement of hydrogen makes this an energy intensive process. Thus, the production of liquid fuel through a cyclic process is considered, consisting of conversion of natural gas and biomass into syngas. The uniqueness of this process is that it does not require any external input of hydrogen but still efficiently convert every carbon atom into carbon monoxide. Natural gas is reacted with alumina in nitrogen atmosphere causing carbothermal reduction of alumina to produce aluminum nitride, hydrogen and carbon monoxide. Aluminum nitride is further hydrolyzed using a catalyst to produce alumina, nitrogen and hydrogen. The first two products are recycled while hydrogen is combined with carbon monoxide to yield syngas in hydrogen/carbon monoxide ratio of two. The excess hydrogen produced is used to convert biomass through the available efficient hybrid hydrogen carbon or catalytic partial oxidation methods.

Keywords: natural gas, biofuels, hydrogen, syngas

1. Introduction

The world's energy system is highly dependent on fossil fuel at the moment. From the transportation sector to the home appliances, everything runs on either liquid hydrocarbons or their derivatives which in turn are primarily derived from coal, gas and oil.

The decline in the availability of oil has led to the development of processes concerning alternative energy resources like biomass, nuclear, wind, water, solar etc. These energy resources except for nuclear energy can be classified mainly as renewable and non-renewable. Non renewable resources such as coal, gas and oil takes very long time of the order of millions of year to convert sunlight into fuel. Fossil fuels can be thought of as old biomass. Plants, animals and other living organisms that died a million of years ago got transformed into fossil fuel by the action of sunlight. On the other hand renewable resources like biomass, wind, wave, hydroelectricity, solar and geothermal convert the solar radiation into useful energy in a far shorter time. This is the reason that the reserves of oil, coal and gas are getting diminished to answer the increasingly energy need of the humans and thus alternative renewable energy resources are being explored.

One such energy source that has drawn attention is biomass [1, 2]. There are basically two aspects associated with biomass – production of biomass and conversion to fuel. Although growing biomass that is cheaper and takes less time to grow have been explored, the efficient conversion to fuel i.e. 100 percent conversion of carbon atom into desirable product is still matter of concern. Almost all the processes used earlier included significant carbon loss in the form of carbon dioxide [1, 2]. This led to twofold disadvantage of losing on carbon and generation of undesirable carbon dioxide which needs to be sequestered and it has potential dangers associated with it. More recently, efficient conversion processes have been proposed but all of such processes need hydrogen [3, 4, 5, 6]. In this study, an effort is made towards efficient conversion without any use of external hydrogen.

2. Solution

To overcome the external hydrogen requirement for the efficient production of biofuel, an alternative pathway that, at the same time, also converts natural gas into syngas has been suggested. The fundamental is to convert natural gas and biomass by two different processes. The conversion of natural gas is employed in such a way that the process produces extra hydrogen than the required which is determined by 2:1 hydrogen to carbon monoxide molar ratio.

The natural gas is converted to carbon monoxide and hydrogen through carbothermal reduction of alumina in a nitrogen atmosphere. Although this process has also been studied earlier [7], its coupling with biomass conversion has not been explored till now. It produces aluminium nitride which is hydrolysed in presence of catalyst to produce the extra hydrogen required. The other products namely alumina and nitrogen are recycled back to the reduction reaction.

The last step is to convert biomass for which various methods like hybrid hydrogen carbon [3] and catalytic partial oxidation [4] methods have already been proposed. The extra hydrogen required is obtained from the above step; for every carbon mole in natural gas that is converted to syngas, one mole of extra hydrogen is produced which is the source of hydrogen required for efficient conversion of biomass.

2.1. Natural Gas treatment to produce syngas

Natural gas, considered to be mostly methane, is reacted with alumina in the presence of nitrogen. This reaction has been carried out experimentally and is also extensively studied in terms of its thermodynamics and kinetics [7, 8]. It produces hydrogen and carbon monoxide in the molar ratio 2:1 desired for the fuel production.

$$Al_2O_3 + 3CH_4 + N_2 \rightarrow 2AlN + 6H_2 + 3CO \qquad \text{(reaction -1)}$$

It is an endothermic reaction and can be carried out easily using a solar reactor. Thus this process does not release any carbon dioxide or any other pollutant into the atmosphere which may have been the case if energy for any endothermic reaction is provided by combustion of fossil fuels. The study of reducing alumina in nitrogen atmosphere in a graphite crucible solar reactor is available elsewhere [9, 10].

The thermodynamic chemical equilibrium has also been carried out. The results obtained are shown in the figure 1. It shows the equilibrium concentration at 1 bar and as a function of temperature of the reactants and products for the reaction. The methane starts to breaks down into carbon at around 200 ^oC which reduces alumina into aluminium nitride and thus produces carbon monoxide. The methane cracking gets completed by 600 ^oC and reduction by 1900 ^oC. A small amount of oxygen measuring approximately 0.05 moles per 3.0 moles of methane is also introduced to minimise any undesirable presence of solid carbon and alumina in the products.

2.2. Production of extra hydrogen

Aluminium nitride produced in the above reaction is hydrolyzed in the presence of catalyst as per the following reaction.

$$2AlN + 3H_2O \rightarrow Al_2O_3 + 3H_2 + N_2 \qquad \text{(reaction -2)}$$

The thermodynamic equilibrium analysis for the reactants and probable products is studied [7]. The results obtained for the chemical equilibrium composition in the absence of catalyst is shown in the figure 2. It illustrates that nitrogen and hydrogen are the stable products for any temperature above 250 ^oC and no stable ammonia must be formed. However it has also been suggested that ammonia may be present in metastable state in the absence of catalyst but high temperature favours decomposition of ammonia into hydrogen and nitrogen. Thus carrying out the reaction at high temperature around 1200 ^oC in presence of supported nickel catalyst produces the desired products including hydrogen [11]. Alumina and nitrogen formed in the reaction are recycled back to the reaction where reduction of alumina is carried out while extra hydrogen produced is used for the conversion of the biomass.

2.3. Conversion of biomass

The conversion of biomass to syngas in order to produce fuel can be obtained through available methods like hybrid hydrogen carbon, reactive flash volatilization or catalytic partial oxidation [3, 4, 5, 6]. The basic of these processes is to suppress the formation of carbon dioxide while treating biomass. To reconvert that carbon dioxide into carbon monoxide, hydrogen is required to carry out the reverse water gas shift reaction. These processes, thus, require external input of hydrogen to efficiently convert carbon atom of biomass into carbon monoxide. The hydrogen is obtained from external sources like inexpensive hydrocarbon rich in hydrogen such as natural gas or biomass or by converting solar energy to hydrogen via the photovoltaic/electrolyser route. However the hydrogen in the solution proposed is obtained through hydrolyses of aluminium nitride which is an intrinsic part of the process.

Though the natural gas treatment and biomass treatment proposed in the solution have been cited earlier but the solution proposed is expected to have much more broader impact since it couples both the process via generation of extra hydrogen in one which is used in the other. The idea is more encompassing and answers for the extra need of the hydrogen. The coal can also be treated in a similar way as natural gas but it would produce just the required hydrogen i.e. 2:1 molar ratio of hydrogen/carbon monoxide. This would result in efficient conversion of coal but will not produce any extra amount of hydrogen. The future research may focus on developing more methods for coal, natural gas or biomass conversion to syngas that will require less additional hydrogen required for combined efficient conversion.

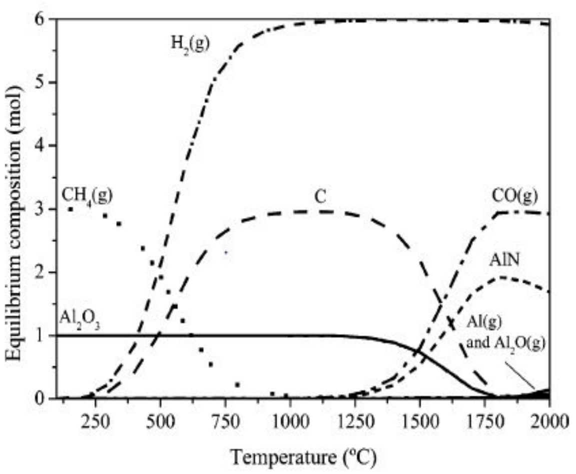

Fig. 1: Equilibrium composition for reaction-1

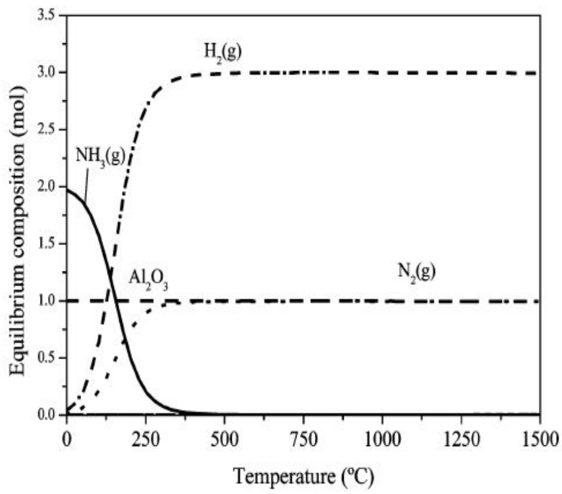

Fig. 2: Equilibrium composition for reaction-2

3. Acknowledgements

The author gratefully acknowledges Dr. Abhijit Chatterjee, Assistant Professor, Department of Chemical Engineering, IIT Kanpur for his motivation and valuable suggestions on this study.

4. References

[1] A. V. Bridgwater *Chem. Eng. J.*, 2003, **91**, 87–102.

[2] C. Schubert, *Nat. Biotechnol.*, 2006, **24**, 777–784.

[3] R. Agarwal, N. Singh, F. Ribeiro and N. Delgass *Proc Natl Acad Sci USA*, **104** 12 (2007), pp. 4828–4833.

[4] J. Colby, P. Dauenhauer, B. Michael, A. Bhan and L.D. Schmidt *Green Chem*, **12** (2010), p. 378.

[5] P. J. Dauenhauer, B. J. Dreyer, N. J. Degenstein and L. D. Schmidt, *Angew. Chem., Int. Ed.*, 2007, **46**, 5864–5867.

[6] J. R. Salge, B. J.Dreyer, P. J. Dauenhauer and L.D. Schmidt, *Science*, 2006, **314**, 801–804.

[7] M. E. Ga´lvez, M. Halmann, A. Steinfeld *Ind. Eng. Chem. Res*. **2007**, *46*, 2042-2046.

[8] M. E. Ga´lvez, M. Halmann, A. Steinfeld *Ind. Eng. Chem. Res*. **2007**, *46*, 2047-2053.

[9] J. P. Murray, A. Steinfeld, E. Fletcher *Energy* **1995**, *20*, 695-704.

[10] J. P.Murray J. Solar Energy *Eng.* **2001**, *123*, 125-132.

[11] George Thomas and George Parks , Potential roles of ammonia in a hydrogen economy, *US Department of Energy* Feb **2006**, 9-11.