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## Abstract

*The present work reports experimental results concerning the effect of the molar* ratio on conversion of ethanol for hydrogen production by steam reforming. Hydrogen fuel obtained by steam reforming of ethanol can be a strong candidate as a clean energy carrier based on the renewable sources of energy. Kinetic study of ethanol steam reforming over a commercial nickel-alumina ( $Ni/Al_2O_3$ ) catalyst was conducted in a fixed-bed reactor. The effects W/F and various molar ratio of steam to ethanol in the feed were studied. For ethanol, the minimum conversion obtained was around 53% at W/F =98 gm-cat hr/mol) and the maximum conversion was around 89 % at W/F = 475 gm-cat hr/mol). It was found that hydrogen conversion was proportional to the  $H_2O/EtOH$ molar ratio and ethanol was completely converted even at relatively low temperature values. Hydrogen selectivity up to 95% was obtained. The acquired data was fitted to a power-law kinetic model and the kinetic parameters were evaluated. A considerable amount of coke formation was observed during the process; yet, the catalyst showed a negligible loss of activity, exhibiting the feasibility of using this catalyst for ethanol steam reforming. In an attempt to reduce this coke formation, it is suggested that the process may be performed in the presence of hydrogen gas.

Keywords: Hydrogen Production, Ethanol, Steam Reforming, Catalyst, Molar ratio

#### Introduction

The generation of hydrogen for fuel cells from alcohol (methanol/ethanol) is possible through several process alternatives: steam reforming, partial oxidation and a combination of steam reforming and partial oxidation. The combined reforming process is referred to as auto-thermal reforming when operated under adiabatic conditions. Steam reforming of alcohol can yield a product gas containing up to 75% hydrogen while maintaining a high selectivity towards carbon dioxide. The main drawback of the steam

reforming process is that it is relatively slow and endothermic. Endothermic steam reforming of hydrocarbons, favored by industry, operates at high temperatures and requires an external heat source.

Hydrogen has long been recognized as an ideal fuel for power generation systems with virtually zero emissions of air pollutants and carbon dioxide. Hydrogen-based fuel cell power plants are highly efficient and reliable, and generate virtually no undesirable air emissions. The use of hydrogen for fuel cell applications represents one of the most environmentally sound methods for the production of electrical energy and is expected to gain wide usage in the near future for both automotive and small-to-medium scale stationary applications.

#### **Steam Reforming Process**

Catalytic steam reforming of hydrocarbon is a well-known, commercially available process for hydrogen production. Hydrogen production is accomplished in several steps: steam reforming, water gas shift reaction, and hydrogen purification. The steam reforming reaction is endothermic and requires external heat input. Economics favor reactor operation at pressures of 1 - 5 atmospheres and temperatures of the order of 500 to 850 <sup>o</sup>C. The external heat needed to drive the reaction is often provided by the combustion of a fraction (up to 25%) of the incoming natural gas feedstock or from burning waste gases (which contain CO), such as purge gas from the hydrogen purification system.

A high temperature shift reactor operating at about  $350-475^{\circ}$ C accomplishes much of the conversion, followed by a lower temperature ( $200-250^{\circ}$  C) shift reactor, which brings the CO concentration down to a few percents or less. Hydrogen is then purified. The degree of purification depends on the application. For industrial hydrogen, pressure swing absorption (PSA) systems or palladium membranes are used to produce hydrogen at up to 99.99 % purity. For proton exchange membranes (PEM) or phosphoric acid fuel cells closely coupled to reformers, diluents such as CO<sub>2</sub> and CH<sub>4</sub> are tolerable. However, CO must be reduced to less than about 10 ppm for PEM fuel cells, so a CO removal system (such as preferential oxidation unit) must be used.

## **Generalised Reactions**

Steam reforming:

$C_mH_n + mH_2O \rightarrow mCO + (m + (1/2) n)H_2 \dots$	(1)	
$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$	(2)	
Carbon formation		
$C_m H_n \longrightarrow xC + C_{m-x} H_{n-2x} + xH_2 \dots$	(3)	
$2CO \rightarrow C + CO_2$	(4)	
$CO + H_2 \rightarrow C + H_2O$	(5)	
Water-gas-shift		
$CO + H_2O \rightarrow CO_2 + H_2$	(6)	
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$CO_2 + H_2 \rightarrow CO + H_2O (RWGS)$	(7)
CO oxidation	
$CO + 1/2 O_2 \rightarrow CO_2 \dots$	(8)
$H_2 + 1/2O_2 \rightarrow H_2O$	(9)

# **Catalyst Characterization**

Without the right catalyst, many reactions hardly proceed. Furthermore, the chemical nature of the catalyst can have a radical effect in selecting reaction pathways leading to different chemical products. The present work focuses on the study and characterisation of the catalyst for steam reforming of hydrocarbons. M/s. Bharat Petroleum Corporation Limited, Mumbai, has supplied the catalyst. Attempts have been made to study the catalyst characterisation using the techniques such as, Scanning Electron Microscope, X-Ray Diffraction. The BET surface area has been found out using Micromeritics surface area analyzer.

## **Experimental Section**

# Feedstock

The infrastructure of INDIA is based on agriculture; hence raw materials, such as cassava, molasses, and corn, are available for fermentation to produce dilute ethanol solution. There are many ways to utilize concentrated ethanol especially as a fuel source e.g. gasoline blender. To obtain high concentration of ethanol, however, the dilute solution of ethanol from fermenter must be dehydrated to a very low moisture content product. Distillation and azeotropic separation contributed to the shortcomings of ethanol as a fuel. [1] The massive use of fuels derived from crude oil is a key factor in the environmental pollution problems and the world looks with increasing interests to enforce research activities on the development of alternative fuels. In this aim, one of the most interesting, ethanol that can be easy produced by fermentation of the starch contained product.<sup>[2]</sup> To identify the challenge in the development of electrical vehicles, literature was rapidly reviewed. Research on hydrogen production processes suitable for fuel cell applications is major challenge. Catalytic steam reforming hydrocarbons as well as alcohol is very promising route. [3] In the last few years, it has been paid much attention to ecological problems related to environment concerns. The efforts have led the research to orient toward alternative solutions as clean and renewable energies, particularly bioenergy. This bioenergy can be obtained from biomass or from other natural sources. Specific work on the hydrogen production has been investigated from mixtures of EtOH-H<sub>2</sub>O for fuel cells. [4] A new promising way to utilize the dilute solution of ethanol is the reforming process of ethanol to produce hydrogen gas that can then be passed through a molten carbonate fuel cell (MCFC) to generate electricity.

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# **Experimental Setup**

The overall flow system consisted of the main parts such as Feeding system, Preheated cum mixer, Reactor, Condenser and cooling system, Sample collecting section, Gas analysis section



Figure 1 Schematic flow diagram of steam reforming unit.

# **Experimental Procedure**

Ethanol solution was prepared by diluting 99 % Ethanol (Lab grade provided by Jiangsu Huaxi international trade Co.Ltd.) with demineralised water. The reforming catalyst, nickel supported on alumina, a commercial product of a catalyst used. It was crushed into small granules with 1 mm size. The experiment was carried out in a 1.27 x 32 cm (diameter x length) fixed bed reactor made of 316-stainless steel and assembled with fittings. The experimental setup to carry out the steam reforming of feedstock (Ethanol) is shown in Fig. 1. The reactor and the preheaters were first allowed to attain a steady temperature as per the required operating parameters. Then the prepared ethanol solution was fed by electromagnetic dosing pump, to a temperature controlled pre-heater unit. The pre-heater unit vapourised the methanol and ethanol solution prior to sending further to the temperature controlled reactor unit. A thermocouple was located in the catalyst bed. The reactor was heated by a high-resistance electric coil. The steam reforming reaction along with other side reactions takes place inside the reactor where a bed of



catalyst is placed at the desired reaction temperature. The reaction product comes out from the bottom of the reactor through a needle valve. The product gases coming from the reactor are cooled and condensed; two U-shape gas sample tubes were used to gather the liquid. The gas was vented out. After condensation, a sample of gas is directly fed to the GC to get analysed. Gas samples were withdrawn every 5 min and then sent to the GC for analysis. Each run was stopped after 30 minutes of operation from the point of feeding the preheater.

#### **Results and Discussion**

## **Catalyst Characterization**

## Specific Surface Analysis Using BET (BET SSA)

The BET surface area has been found out using Micromeritics surface area analyzer. BET surface area for 1 mm particle was found 12.4 m<sup>2</sup>/g. From literature [10] the value of SSA for Ni/Al<sub>2</sub>O<sub>3</sub> has been reported as 14-42 m<sup>2</sup>/g.

## Elemental analysis using X-Ray Diffraction method (XRD)

The XRD analysis was performed to determine the bulk crystalline phases of the nickel species in the catalysts. XRD patterns were collected with a Rigaku-Miniflex diffractometer using monochromatised Cu K $\alpha$  radiation. The spectra were scanned from  $2\theta = 10^{0}$  to  $80^{0}$  at a rate of  $2^{0}$ /min ( $2\theta$ ). From the data obtained Crystalline or amorphous form was found having the cubic structure Dimension and unit cell structure parameter (a) = 8.048 A<sup>0</sup>. The diffraction profile is related to the size and perfection of the crystallizes and various instrumental parameter. The intensity versus  $2\theta$  curves are as follows



Figure 2 Intensity vs  $2\theta$  curve for catalyst of size 1 mm



# Surface Study Using Scanning Electron Microscopy (SEM)

The following structures were observed using SEM photograph as shown in figure 3 for catalyst of 1mm sizes at magnification x 1000. From the photograph it is observed that there is no significance change in the micro structural appearance of the catalyst.



Figure 3 Photographs for catalyst 1mm sizes at magnification x 1000

# Effect of molar ratio on Conversion



Figure 4 Variation of conversion of ethanol with W/F at two different molar ratios.

For ethanol the minimum conversion obtained 53% (3500 C, W/F =98 gm-cat hr/mol) and the maximum conversion was found 89 % (525 0C, W/F = 475 gm-cat hr/mol) with increase in both temperature and W/F. The reported conversions are higher compared to the current results. In addition,



the temperature for reforming is reported to be lower than the present study. For steam reforming of ethanol, a limited number of data are available in the literature. The reported conversion [5, 6] for reforming on Ni/Al2O3 catalyst is in the range of 80-95 %. It may be noted that the values of conversion in this study are similar. However, the values of temperature and W/F are higher. Therefore it can be inferred that this Ni/Al2O3 catalyst is suitable for ethanol steam reforming; however further studies are required to optimize operating parameters.[7]

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