

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Processes of Hydrogen Production

The inter-related problems of energy and environment are among the biggest challenges facing the world today, in particular energy sustainability and carbon emissions from the fossil fuels. Hydrogen has been projected as one of the few long-term sustainable clean energy carriers, emitting only water vapor as a by-product during the combustion or oxidation process

There are several established and developing technologies to produce hydrogen from various sources. For example, CO₂ free hydrogen production can be achieved through methane decomposition and methane aromatization. Steam reforming, partial oxidation and autothermal reforming of hydrocarbons such as natural gas, as well as the shift reaction of gaseous products of coal gasification.

2.2 Pyrolysis of Biomass

Pyrolysis is the thermal decomposition of biomass occurring in the absence of oxygen. It is the fundamental chemical reaction that is the precursor of both the combustion and gasification processes and occurs naturally in the first two seconds. The products of biomass pyrolysis include biochar, bio-oil and gases including methane, hydrogen, carbon monoxide, and carbon dioxide. Depending on the thermal environment and the final temperature, pyrolysis will yield mainly biochar at low temperatures, less than 450 °C), when the heating rate is quite slow, and mainly gases at high temperatures, greater than 800 °C), with rapid heating rates. At an intermediate temperature and under relatively high heating rates, the main product is bio-oil.

Pyrolysis can be performed at relatively small scale and at remote locations which enhance energy density of the biomass resource and reduce transport and handling costs. Pyrolysis offers a flexible and attractive way of converting solid biomass into an easily stored and transported liquid, which can be successfully used for

the production of heat, power and chemicals. A wide range of biomass feedstock can be used in pyrolysis processes. The pyrolysis process is very dependent on the moisture content of the feedstock, which should be around 10%. At higher moisture contents, high levels of water are produced and at lower levels there is a risk that the process only produces dust instead of oil. High-moisture waste streams, such as sludge and meat processing wastes, require drying before subjecting to pyrolysis.

The efficiency and nature of the pyrolysis process is dependent on the particle size of feedstock. Most of the pyrolysis technologies can only process small particles to a maximum of 2 mm keeping in view the need for rapid heat transfer through the particle. The demand for small particle size means that the feedstock has to be size-reduced before being used for pyrolysis. Pyrolysis processes can be categorized as slow pyrolysis or fast pyrolysis. Fast pyrolysis is currently the most widely used pyrolysis system. Slow pyrolysis takes several hours to complete and results in biochar as the main product. On the other hand, fast pyrolysis yields 60% bio-oil and takes seconds for complete pyrolysis. In addition, it gives 20% biochar and 20% synthesis gas. Bio-oil is a dark brown liquid and has a similar composition to biomass. It has a much higher density than woody materials which reduces storage and transport costs.

2.3 Acetic Acid from Bio-oil

The aqueous phase of the bio-oil consists of 20% organics and 80% water. Main components of bio-oil in organics phase belong to the following groups: acids, aldehydes, alcohols, ketones, phenols, sugars, and furans as showed in Table 4.1. Phenolic compounds are derived from lignin, whereas the rest components are mainly obtained from cellulose and hemicelluloses. Acetic acid is one of the major components of bio-oil (up to 12%). Acetic acid itself is renewable and can be easily obtained from biomass by fermentation process. In addition, acetic acid is noninflammable unlike methanol and ethanol; hence it is a safe H₂ carrier and chosen as a model compound representing all acid in bio-oil.

Table 2.1 Composition of bio oil aqueous phase

Component	Range (wt%)
Formic acid	4-8
Acetic acid	8-12
Hydroxyacetaldehyde	5-10
Hydroxyacetone	8-12
Furfural	2-5
2-Furanone	2-5
Glucose	15-20
Levogluconan	15-20
Guaiacol	4-8
Water	15-20
Other	0.5-1

2.4 Steam Reforming

The most common method of "on-purpose" hydrogen production is the steam reforming process from natural gas and other hydrocarbons. Steam reforming is processes where hydrocarbons react with steam on a catalyst at high temperatures where by the hydrocarbons are converted to CO and H₂. The steam reforming is normally accompanied by the water gas shift (WGS) and the methanation reaction, where the extents of these reactions depend on the operating conditions. The reforming, WGS, and methanation reactions are shown below (Equations 2.1-2.3).



The reforming reaction is endothermic reaction while the methanation and WGS is exothermic. The reforming equilibrium is favored by high temperatures and low pressures, while the WGS is shifted toward carbon monoxide (CO) and water (H₂O) at high temperatures. The reforming reaction (Equation 2.1) is not reversible

over most SR catalysts at the reaction conditions usually employed. On the reforming of methane utilizes two simple reversible reactions. The first step of the reaction is the decomposition of methane and the second step is the water-gas shift reaction.

2.4.1 Decomposition of Methane

The first step of the methane steam reforming involves methane reacting with steam at 750-800°C to produce a synthesis gas which give a more favorable H₂/CO ratio of some application (Equation 2.1).



This reaction is highly endothermic which requires heat and catalyst. Catalyst used in this reaction typically is nickel at pressures in the range of 15 to 30 atm and at high temperature from 850 to 900 °C. This reaction causes a higher yield of hydrocarbon by using iron (Fe) or chromium (Cr) oxide catalyst. The ratio of steam/methane in feed mixture is usually higher than unity in order to avoid carbon and excess carbon monoxide formation.

2.4.2 Water-Gas Shift Reaction

The second step is water-gas shift reaction (WGSR) (Equation 2.5) constitutes an integral part of the reforming which is exothermic reaction. The carbon monoxide derived from the first reaction reacts with steam over a catalyst producing hydrogen and carbon dioxide (CO₂). This process occurs in two stages, consisting of high temperature shift (HTS) at 350 °C and a low temperature shift at 190 to 210 °C.



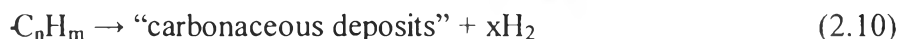
As a result of exothermic reaction of this reaction, it is possible to get high energy efficient heat by recovering and recycling heat to use in the first stage with heat exchanger but resulting in higher cost of production for heat exchanger.

The other side reaction that occurs in steam reforming is methanation reaction of CO and CO₂ (Equations 2.6-2.7).



Both water-gas shift (Equation 2.5) and methanation (Equation 2.6-2.7) reaction occur simultaneously. Moreover, there also are some side reactions

such as methane decomposition (Equation 2.8), and carbon monoxide disproportionate or the Boudour reaction (Equation 2.9).



The last two reactions cause the carbon deposition on the catalyst which occurs in the form of filament and encapsulating carbon leading to the deactivation of catalytic activity and clogging of the reforming reactor

At high temperature (above 650 °C), the hydrocarbons may react in parallel to steam reforming by thermal cracking into olefins which may easily form coke (Equation 2.8 and 2.10). The carbon deposition on the catalyst causes operational troubles which occur in the form of filament and encapsulating carbon leading to the deactivation of catalytic activity, increase of pressure drop and clogging of the reforming reactor.

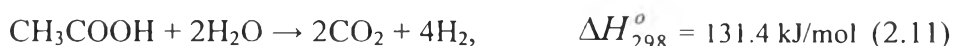
Catalytic steam reforming of methane has efficiency about 80% which is the highest of currently commercial production and the need of heat recycling is mainly caused the high cost in this process.

2.5 Steam Reforming of Acetic Acid

The study on steam reforming of acetic acid can be accomplished with different supported metal catalysts in a temperature range of 500–750 °C.

Steam reforming of acetic acid is quite complex and may be represented by the following stoichiometries (Basagiannis *et al.*, 2006).

The overall steam reforming reaction:



Bio-oil components are in general thermally unstable at the typical temperatures of the reformer. As a result, thermal decomposition (cracking) for most oxygenates can occur forming mainly coke and a mixture of gases as described in the following reactions:





Ketonization



After thermal decomposition, steam reforming of CH_4 , water gas shift reaction (WGSR), methanation of CO and CO_2 and the Boudourd reaction are also included.

At mild temperatures, methanation of CO and CO_2 are preferred in steam reforming due to the high concentration and favorable reaction temperatures of CO , CO_2 and H_2 in products. For high temperatures, methane steam reforming initiates converting methane to hydrogen.

2.5.1 Catalysts used in Steam Reforming

The catalytic performance a variety of supported metal catalysts was investigated, noble metal such as Rh, Pd, and Pt, or base metal like Ru and Ni on alumina (Al_2O_3) support were compared the catalytic activity for acetic acid conversion at a relatively high temperature (at 750°C) by turnover frequency (TOF), which is activity expressed per exposed atom (metal loading for each metal catalyst was not the same). Ni exhibits the higher intrinsic activity per exposed atom among all investigated catalysts while Pt is the lowest, the rank based on their activity seems to be as following; $\text{Ni} > \text{Rh} > \text{Ru} > \text{Pd} > \text{Pt}$. (Basagiannis *et al.*, 2007).

The Ni metallic phase supported metal oxides such as $\alpha\text{-Al}_2\text{O}_3$, $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$, and MgO were tested under the steam reforming of acetic acid (Thaicharoensutcharittham *et al.*, 2011). It was found that the catalytic activity and carbon formation for the catalysts studied were significantly dependent on the Ni content and the nature of support. The 15%Ni/ $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ catalyst exhibited the highest catalytic performance in terms of C–C breakage conversion and hydrogen yield. In addition, the redox property of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ provided higher stability than the MgO and $\alpha\text{-Al}_2\text{O}_3$ due to its less carbon deposition even at low steam-to-carbon ratios. At a high steam to carbon ratio ($\text{S/C} = 6$), the effect of the support on the ac-

tivity was found to be less pronounced but was still present on the carbon formation of the catalysts.

Many different catalytic systems have been investigated (Trane *et al.*, 2012) and the most promising metals seem to be Ni, Rh, or Ru. Ni is preferred if the catalyst can achieve good performance with respect to initial conversion and yield of hydrogen, but the main problem is that the catalysts are not stable over longer periods of operation (>100 h) due to carbon deposition. Support materials consisting of a mixture of basic oxides and alumina have shown the potential for low carbon formation and promotion with K is beneficial with respect to both activity and carbon formation. The coke formation appears to be less significant in fluidized beds. The addition of O₂ to the system can decrease the coke formation and provide autothermal conditions at the expense of a lower H₂ and CO-yield.

The catalytic activity for steam reforming of acetic acid was investigated over Ni/Ce_{0.75}Zr_{0.25}O₂ and Co/Ce_{0.75}Zr_{0.25}O₂ catalysts (Phongpreuksathat, 2013). The results showed that Ni/Ce_{0.75}Zr_{0.25}O₂ exhibited higher catalytic activity for hydrogen yield throughout the range of steam to carbon ratios and temperature investigated due to a better acetic acid cracking and water gas shift activity. Moreover, the apparent activation energy can be used to confirm that steam reforming occurred with a higher rate over Ni/Ce_{0.75}Zr_{0.25}O₂ but with lower rate in reverse water gas shift reaction. It was also found that Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst was much more stable than Co/Ce_{0.75}Zr_{0.25}O₂ catalyst which was deactivated rapidly due to carbon formation and oxidation of Co metal.

2.6 Partial Oxidation

Catalytic partial oxidation (CPOX) is an attractive option to produce H₂ and CO from hydrocarbon fuels for fuel cell applications. CPOX can also be followed by the water gas shift (WGS) reaction to produce a pure H₂ stream. CPOX has the advantage of inherently rapid reforming kinetics with quick light-off characteristics and response to transients. Additionally, the exothermic nature of this process reduces the heat needed to be supplied to the system, making it ideal for integration with high temperature fuel cells. The process is applicable to various feedstocks ranging from

natural gas to heavy oil. Challenges for the CPOX of hydrocarbons include catalyst deactivation from high-temperature sintering, metal vaporization, support degradation, coke formation, and poisoning from sulfur and other contaminants. The reactions occurring in the CPOX of hydrocarbons are complex. The overall CPOX reaction can be described by

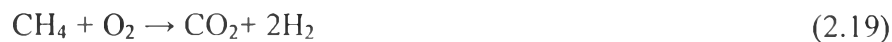


For methane partial oxidation is widely industrial-used process for converting methane into synthesis gas. There are many reaction and side reactions can occur as see in following reaction.

Catalytic partial oxidation



Combustion



Water gas shift



Steam reforming



CO₂ reforming



Methane decomposition



Boudouard



The most significant side reactions are the WGS (Equation 2.20), SR (Equation 2.21), and CO₂ reforming (Equation 2.22), which help determine the final synthesis gas composition. This composition will vary based on the hydrocarbon fuel used and the reaction conditions selected. Typical operating conditions provided are the temperature range of 700-1,000°C, atmospheric pressure, oxygen-to-carbon

(O/C) ratio = 1.2, and the gas hourly space velocity (GHSV) range from several thousands to several hundred thousand $\text{scc g}_{\text{cat}}^{-1} \text{h}^{-1}$. (Enger *et al.*, 2008)

2.6.1 Catalysts used in Partial Oxidation

Otsuka *et al.* (1999) investigated a series of $\text{CeO}_2\text{-ZrO}_2$ composite oxide ($\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$) for the gas-solid reaction with CH_4 in the absence of gaseous oxidant. They reported that at Zr content below 50 at%, the $\text{CeO}_2\text{-ZrO}_2$ solid solution still showed the fluorite structure and no change in degree of reducibility. $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ provided synthesis gas with a H_2/CO ratio of 2 and higher in producing rate and lower activation energy than CeO_2 due to the incorporation of ZrO_2 into CeO_2 this caused the mobility of lattice oxygen to increase. Moreover, they reported the effect of presence of Pt that enhancing the reaction rate.

Takeguchi *et al.* (2001) studied the performance of $\text{Ni/CeO}_2\text{-ZrO}_2$ catalysts for the partial oxidation of methane to synthesis gas. They reported that the catalytic activities of the $\text{Ni/CeO}_2\text{-ZrO}_2$ catalysts for the partial oxidation reaction of methane increased with increasing of oxygen storage capacity of the $\text{CeO}_2\text{-ZrO}_2$ solid solution indicating that this reaction proceeded by means of the redox mechanism. Furthermore, they also reported that Ni particles that having weak interaction with the support showed large amount of coke whereas the nickel particles having a strong interaction showed small amount of coke.

Roh *et al.* (2002) studied the synthesis gas production by steam reforming of methane and reported that 15%Ni/Ce-ZrO₂ exhibited the best activity and stability. This high performance resulting from the combination of high oxygen storage capacity of ceria in Ce-ZrO₂, strong interaction between Ni and Ce-ZrO₂, basic properties of the catalyst and high capability of H₂ uptake.

There was the investigated on the effect of different CeZrO_2 loadings on the catalytic properties and performance for POM reaction over $\text{Pt/x\%CeZrO}_2/\text{Al}_2\text{O}_3$ catalysts ($x=0\text{--}40\text{wt.}\%$) (Fabiano *et al.*, 2012). The characterization results showed that both BET surface areas and metallic dispersions did not varied significantly with the increase of the ceria-zirconia mixed oxide content. However, XRD results indicate that, for samples containing 10 and 20wt.% of CeZrO_2 , there was the formation of a homogeneous solid solution. On the other hand, for catalysts containing higher ceria-zirconia loadings (30 and 40wt. %), the

solid solution formed was not homogeneous, with evidence of an isolated zirconia phase. During catalytic tests, initially all the samples presented similar activities. Over the reaction period, Pt/Al₂O₃ and the samples containing 30 and 40wt.% of CeZrO₂ deactivated, with H₂ and CO selectivities dropping and CO₂ formation increasing. On the other hand, the samples with a homogeneous ceria–zirconia solid solution (Pt/10%CeZrO₂/Al₂O₃ and Pt/20%CeZrO₂/Al₂O₃) remained quite stable during TOS, which is likely due to high oxygen mobility in the lattice, which helped to keep the surface of the catalysts free of carbon deposits.

2.7 Coke Formation

The high temperatures associated with steam reforming to produce hydrogen also favor the formation of carbon (Trimm, 1997). Four reactions may be involved



Reactions (2.28) - (2.30) are reversible. It is possible to estimate minimum steam/carbon or carbon dioxide/carbon ratios to avoid coke formation during reforming. If coke is formed, it may originate from several sources. Because of the high temperatures of reaction, coking may result from gas phase reactions leading to carbonaceous intermediates which condense on a surface. The reactions involve free radical polymerizations and the addition of diluents such as steam reduces their importance. Nonetheless, gas phase coke can accumulate on the catalyst, particularly with heavier hydrocarbon feedstocks. The carbon may be gasified, may encapsulate the surface or may dissolve in the nickel crystallite. The dissolved carbon diffuses through the nickel to nucleate and precipitate at the rear of the crystallite. This continuing process leads to the formation of a carbon whisker, which lifts the nickel crystallite from the catalyst surface, and eventually results in fragmentation of the catalyst. Nonetheless, the formation of carbon whiskers can lead to build up of pressure in the catalyst bed as a result of catalyst fragmentation and coking.

2.7.1 Strategies for Coke Minimization:

It is possible to calculate limits based on the ratio of carbon in the feedstock to steam or carbon dioxide beyond which carbon will not be formed. This provides a very useful guide to desired operating conditions, but the penalties associated with the economics of superheating reagents are very real.

There are a lot of catalysts using in industry for minimizing carbon formation, nickel is not the most effective catalyst for steam reforming. Both ruthenium and rhodium are more effective catalysts on which carbon formation appears to occur via a different mechanism. The major coking problem with nickel arises because of the formation, diffusion and dissolution of carbon in the metal. Neither ruthenium nor rhodium dissolves carbon to the same extent and, as a result, carbon formation is less in these systems. Despite this attraction, the cost and availability of precious metals is such that such catalysts are not used widely in industrial applications.

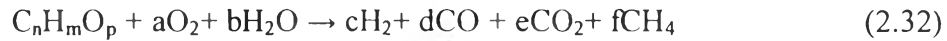
It has been demonstrated that minimal coking can be observed during steam reforming if traces of sulphur are added to the feed. There is a necessity closely to control the presence of sulphide in the feed to levels that are sufficient to create correct size ensembles but not to poison totally the surface. The benefit to be obtained makes such control more than worthwhile.

Furthermore, from many research found another way to reduce coke formation by adding O_2 into steam reforming process that could help to reduce coke formation such as oxidative steam reforming of ethanol over Pt/CeZrO₂ (Sania *et al.*, 2008), oxidative steam reforming of methane (Juliana *et al.*, 2011).

2.8 Autothermal Steam Reforming

Oxidative steam reforming (OSR) is a combination of steam reforming (SR) and partial oxidation (POX) and consideration as it is a combination of the endothermic steam reforming reaction and the exothermic partial oxidation process. This process requires less energy and helps reduce the amounts of methane and coke produced while providing a high H₂ yield and a low CO yield. Moreover, the combination of these reactions can improve the reactor temperature control and reduce the

formation of hotspots, avoiding catalyst deactivation by sintering or carbon deposition (Qi *et al.*, 2005) Oxidative steam reforming (OSR) can be expressed by the following general Eq. (6.1):

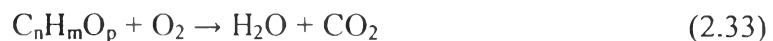


As seen from Eq. (2.32), Co-feeding air and steam together utilizes the heat generated from exothermic oxidation of the fuel to promote the endothermic steam-reforming reactions. In fact, a unique operating condition exists for all fuels in which the heat from the oxidation reactions thermally balances the endothermic steam reforming reactions, rendering the overall reaction thermoneutral. This is called autothermal reforming (ATR). Optimal operating conditions for OSR have been determined to be O/C ratio = 0.7-1.0, steam-to-carbon ratio (S/C) = 1.5-2.0, and temperatures roughly around 700-800°C (Ni *et al.*, 2006).

2.8.1 Contributing Reaction

The autothermal steam reforming reaction consists of a complex series of sub-reactions which have their own intrinsic kinetic dependence on temperature, and local species concentration in the reactor. OSR is the net sum of all these reactions that is rich in H₂ and CO. The key reactions responsible for the eventual production of synthesis gas are presented below (Daniel J *et al.*, 2011).

Complete oxidation



Incomplete oxidation



Partial oxidation



Steam reforming



Dry reforming



Water-gas shift



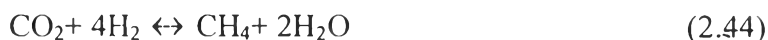
Some major undesirable side reactions that occur, which reduce selectivity to H_2 are: Hydrogen oxidation



Carbon monoxide oxidation



Methanation



Reverse water-gas shift



Reaction conditions for OSR can also promote the little formation of carbon, which is another undesirable reaction product. Carbon accumulation can lead to uneven heat transfer, blocked or constrained flow through the reactor, as well as catalyst deactivation. Listed below are several routes for carbon formation:

Decomposition



Boudouard

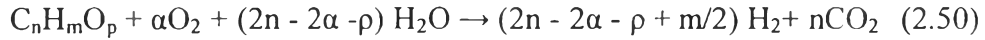


Hydrogenation of CO and CO_2



2.8.2 Autothermal Operation

The following method developed by Krumpelt *et al.*,(2001) can be used to estimate the O/C and S/C ratios for ATR operation. As stated earlier, the generalized stoichiometry for the OSR reaction can be represented by Equation (2.32). The maximum amount of H_2 can be obtained from this reaction if it is assumed that a stoichiometric amount of steam is present to convert all carbon-containing species to CO_2 as shown by the following expression.



Based on reaction stoichiometry, the maximum amount of H_2 formed is the stoichiometric coefficient $2n - 2\alpha - \rho + m/2$. The reaction enthalpy corresponding to the stoichiometric reaction shown by Eq. (2.50) is then

$$\Delta H_r = n\Delta H_{f,CO_2} - (2n - 2\alpha - \rho)\Delta H_{f,H_2O} - \Delta H_{f,fuel} \quad (2.51)$$

At the ATR point, $\Delta H_r = 0$. Rearranging Eq.(2.51) to obtain the thermoneutral stoichiometric O_2 coefficient, α , gives

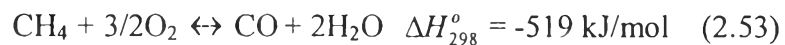
$$\alpha_0 = n - \rho/2 + 1/2 \left[\frac{\Delta H_{f,fuel} - n\Delta H_{f,CO_2}}{\Delta H_{f,H_2O}} \right] \quad (2.52)$$

2.8.3 Mechanism

The reaction mechanism is depending on the catalyst, the fuel type, and the reaction conditions applied. The OSR reaction has been mainly described by combustion-reforming mechanism.

Combustion-reforming mechanism under OSR conditions, the hydrocarbon conversion takes place in the following two steps. First, part of the fuel undergoes combustion with forming mainly H_2O and CO_2 as products. A very small section of the catalyst bed is utilized during this step, due to the fast kinetics of combustion. If the reaction takes place according to the stoichiometry, 25% of the fuel is converted during this process by the oxygen. The remaining unconverted fuel fragments are then converted into synthesis gas primarily through endothermic steam reactions down the rest of the catalyst bed. After the initial combustion zone, the equilibrium of the WGS/RWGS also takes place in this region. For methane combustion-reforming mechanism is following (Ruiz *et al.*, 2008).

Combustion reaction of methane:

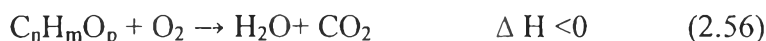


Methane reforming and water-gas shift reaction:



For the combustion-reforming mechanism of higher hydrocarbons can be simplified by similar reactions.

Combustion reaction:



Reforming reactions:

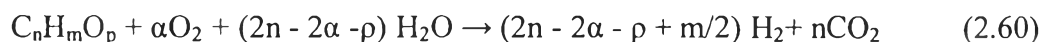


On the study of OSR reaction from combustion-reforming mechanism of n-C₄H₁₀ by varying the contact time (Sato *et al.*, 2009). While running at short contact times (0.15 ms) had high selectivity to CO₂ and low fuel conversion (20%) at O/C=1.0, S/C=1.0, and 450°C using a Ni/MgO catalyst. Increasing the contact time from 0.15 to 1 ms resulted in a decrease in CO₂ selectivity, while improving the selectivities of both H₂ and CO, and also conversion (95%). Collectively these results suggest that the first step in OSR is a highly exothermic combustion reaction, which is then followed by reforming reactions to produce synthesis gas. Also, CO selectivity decreased by increasing the contact time to 10 ms likely due to water-gas shift and methanation reactions.

2.9 Autothermal Steam Reforming of Acetic Acid

According to the composition of bio-oil, acetic acid is one of the major components, non-flammable, it is safe hydrogen carrier. Nevertheless, on studies of steam reforming have been found coke formation and need supplying heat to the reaction system. Moreover, no study on production of hydrogen from acetic acid via autothermal steam reforming.

The autothermal steam reforming of acetic acid the overall reaction is not need energy which can save the energy and can be expressed by following equation (Equation 2.60).



2.10 Catalysts in Autothermal Reaction

The supported catalysts have been widely used in oxidative steam reforming and autothermal steam reforming on hydrocarbons and oxygenated hydrocarbons are CeO_2 , ZrO_2 , Al_2O_3 and CeZrO_2 . The supported catalysts typically used with metals and noble metals.

Ni/CeZrO_2 -based catalysts were investigated in autothermal methane reforming by Dantas *et al.* (2007). The use of alumina propitiated a higher surface area for the samples, which favored the formation of smaller nickel oxide, and metallic nickel particles as observed by XRD and metal dispersion experiments. XRD analysis also revealed the formation of a ceria zirconia solid solution. In general, the catalytic performance of $\text{Ni/CeZrO}_2/\text{Al}_2\text{O}_3$ was better than $\text{Ni/Al}_2\text{O}_3$ and $\text{CeO}_2/\text{Al}_2\text{O}_3$ which may be correlated to the higher reducibility and better redox properties verified for this catalyst.

Catalytic steam reforming of acetic acid in a fluidized bed reactor with oxygen addition was studied (Medrano *et al.*, 2008). The effects of various factors have been studied in fluidized bed steam reforming by use coprecipitated Ni/Al catalysts with acetic acid at $650\text{ }^\circ\text{C}$. First of all, calcinations temperatures of 750 , 850 and $900\text{ }^\circ\text{C}$ have been studied. A lower reforming activity and stability has been observed when using the catalyst calcined at $900\text{ }^\circ\text{C}$, probably due to the increase in spinel phase that is harder to reduce. The incorporation of a Ca/Al ratio of 0.50 under the experimental conditions did not improve the reforming activity and stability. Finally, the influence of oxygen addition to the steam reforming process indicated that an excess of oxygen ($8\text{v/v}\%$) can lead to a lower reforming activity decreasing the H_2 and CO yields and increasing the CO_2 and CH_4 yields but the effect was found to be less pronounced with less oxygen ($4\text{v/v}\%$).

Steam reforming, partial oxidation, and oxidative steam reforming of ethanol over Pt/CeZrO_2 catalyst was studied (De lima *et al.*, 2008). It was found that at a lower operating temperature (773 K), the catalyst was found to deactivate significantly during ethanol decomposition and steam reforming. Adding oxygen to the feed improved the catalyst stability, however it also adversely affected hydrogen selectivity, as a significant fraction of the hydrogen product formed was in turn oxi-

dized to water. For SR, increasing the water/ethanol ratio tended to favor the SR reaction route at the expense of catalyst stability. Increasing the reaction temperature from 773 to 1073 K greatly improved the catalyst stability.

Oxidative steam reforming of ethanol at low oxygen to ethanol ratios was investigated over nickel catalysts on Al_2O_3 supports that were either unpromoted or promoted with CeO_2 , ZrO_2 and $\text{CeO}_2\text{-ZrO}_2$ (Srisiriwat *et al.*, 2009). The promoted catalysts showed greater activity and a higher hydrogen yield than the unpromoted catalyst. The characterization of the Ni-based catalysts promoted with CeO_2 and/or ZrO_2 showed that the variations induced in the Al_2O_3 by the addition of CeO_2 and/or ZrO_2 alter the catalyst's properties by enhancing Ni dispersion and reducing Ni particle size. The promoters, especially $\text{CeO}_2\text{-ZrO}_2$, improved catalytic activity by increasing the H_2 yield and the CO_2/CO and the H_2/CO values while decreasing coke formation. This results from the addition of ZrO_2 into CeO_2 . This promoter highlights the advantages of oxygen storage capacity and of mobile oxygen vacancies that increase the number of surface oxygen species. The addition of oxygen facilitates the reaction by regenerating the surface oxygenation of the promoters and by oxidizing surface carbon species and carbon-containing products. The increases in ethanol conversion and H_2 yield over all catalysts were favored by increasing the temperature, while the reduction in CO and CH_4 yields was favored by the increasing the O_2 : EtOH ratio.

Effect of different promoters on Ni/CeZrO₂ catalyst for autothermal reforming and partial oxidation of methane was investigated by Dantas *et al.* (2009). This study revealed that the addition of promoters to 10%Ni/CeZrO₂ catalyst did not influence the BET area. 0.1%Ag-10%Ni/CeZrO₂ showed the best redox capacity, due to higher CO and CO₂ desorption in CO₂-TPD. Autothermal methane reforming revealed that among all catalysts, 0.1%Ag-10%Ni/CeZrO₂ presented higher values of methane conversion and stability during the reaction. For partial oxidation of methane, just as observed in autothermal reforming, 0.1%Ag-10%Ni/CeZrO₂ also presented the best performance during the 24 h of reaction and the addition of silver by successive impregnation resulted in a lower methane conversion, probably, due to the smaller values of metal dispersion.

Nickel catalysts supported on Al_2O_3 , $\text{CeO}_2/\text{Al}_2\text{O}_3$, $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2/\text{Al}_2\text{O}_3$, and $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ were investigated for methane oxidative reforming (Dantas *et al.*, 2012). The use of alumina led to higher surface areas which favored larger nickel dispersions. The formation of a ceria zirconia solid solution was observed through XRD analyses, although, for $\text{Ni}/\text{CeZrO}_2/\text{Al}_2\text{O}_3$, the solid solution obtained was not homogeneous. Cerium containing samples showed good oxygen storage capacities. During oxidative reforming of methane, samples supported on alumina showed similar methane conversions, which could be related to similar nickel dispersions. No oxygen was detected at the exit of the reactor. The samples presented good stability during 24 h on stream and high H_2 formation, with a H_2/CO ratio close to the theoretical value for this reaction.

As a result, the use of a support $\text{Ce}-\text{ZrO}_2$, solid solution also has a high oxygen storage capacity which plays the important role of enhancing catalytic activity under reducing and oxidizing conditions. Moreover, zirconia improves the thermal stability of ceria by decreasing the rate of crystallite growth and also this solid solution support has been shown to be useful in keeping the metal free from coke deposits in steam reforming, partial oxidation, and autothermal reforming when using nickel or noble metals as catalysts. On noble metal catalyst is well-known as a high activity and dominant stability but the rareness and high cost of noble metal catalysts so this research will use non-noble catalyst which is $\text{Ni}/\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ catalyst.