CHAPTER II

Literature Review
2.1 Introduction

There are several studies focused on hydrogen production from model bio-oil compounds. Due to the complexity of the bio-oil composition, model compounds have been used to study the process parameters and selection of catalysts for steam reforming of bio-oils. Certainly, model compound studies are useful, due to the fact that they highlight structure-reactivity of bio-oil components. Besides, they provide a systematic approach for determining how best \( \text{H}_2 \) productivity can be maximized while minimizing catalyst coking. There are several studies in bio-oil reforming using various catalysts showing comparative analysis of the performances of different metals and supports. Thermodynamic study on hydrogen generation from different model bio-oil reforming processes has been carried out by Vagia and Lemonidou (2007), Xiea et al. (2011) and Chattanathan et al. (2012) have comprehensively reviewed bio-oil reforming derived from biomass and suggested scope of work in this context.

Depending upon the source of heat and the types of reactants, reforming can be either by steam (steam reforming), or by humidified air (partial oxidation reforming), or by a mixture of air and steam (auto-thermal reforming). There are very few studies which provide an insight for auto thermal and partial oxidation reforming.

Steam reforming is an efficient process for hydrogen production and has been in practice since 1930 (Rostrup-Nielson, 1984). Standard Oil Co., USA began the first steam reforming plant in 1930 with light alkanes as feed (Navarro et al., 2007). The steam reforming process is a catalytic vapour phase reaction. It is an endothermic and hence occurs at high temperatures (>773 K) and low pressures (i.e., 0.1 MPa.) where an oxygenated hydrocarbon reacts with steam in presence of catalyst to form carbon dioxide and hydrogen as their primary products via water gas shift reaction resulting in formation of more CO which is an intermediate product.

\[
C_nH_mO_k + (2n - k)H_2O \rightarrow nCO_2 + (2n + (m/2) - k)H_2
\]  

Eq. 2.1 can also be carried out in the aqueous phase at low temperatures (e.g., 543 K) and high pressures (e.g. 6 MPa). It is known as aqueous phase reforming and was developed by Dumesic and his co-workers. Due to mild reaction temperature, the energy requirement of aqueous phase reforming is lower than that of steam reforming which leads to low levels of CO concentration in the reformate (Shabaker et al., 2004).
Iriondo et al. (2008) used different promoters and found that Ni catalyst does not work very well for glycerol due to severe deactivation. A study by Vispute and Huber (2009) showed aqueous phase reforming of the aqueous fraction of bio-oil for hydrogen production over 1 wt% Pt/Al₂O₃ catalyst.

The partial oxidation process is exothermic in nature. The substrate is oxidised with oxygen (in presence or absence of catalyst) resulting in high temperature which in turn provides the required heat internally. The general reaction for partial oxidation is represented by Eq. 2.2. However, excess air results in complete oxidation of the substrate which forms CO₂ and water (see Adhikari et al., 2009).

\[
(\text{Substrate}) \ C_n H_m O_k + \text{air} \rightarrow \text{carbon oxides} + H_2 + N_2 \quad (2.2)
\]

Marda et al. (2009) conducted noncatalytic partial oxidation of bio-oil and reported low H₂ yield of 25% while Rennard et al. (2008) performed auto-thermal catalytic partial oxidation of bio-oil using esters and acids as model compounds over platinum and rhodium based catalysts and showed the efficiency of synthesis gas production.

Auto-thermal reforming is a combination of steam reforming and partial oxidation reforming techniques where substrate is reformed in presence of air and water to produce H₂. In an analogous manner, no external heat is supplied in this process. It is a combination of endothermic water aqueous/steam reforming and exothermic oxidation. The general reaction for auto-thermal reforming is given by Eq. 2.3.

\[
(\text{Substrate}) \ C_n H_m O_k + \text{air} + \text{steam} \rightarrow CO + N_2 + H_2 \quad (2.3)
\]

The advantage of auto-thermal reforming is the process does not require energy ideally because of heat produced during oxidation step is consumed during steam reforming. Vagia et al. (2008) performed thermodynamic analysis of auto-thermal reforming of selected aqueous fraction to determine the optimum amount of oxygen required to carry out an energy neutral process. They also studied effect of reaction variables like temperature and pressure on H₂ production. Optimum reaction conditions as suggested by their investigation was 1 kmol of H₂ to produce from 0.245 kmol of bio-oil which is 20% lower than H₂ obtained by steam reforming. It is
worthy of note that hydrogen produced in this reaction too is lesser than that in conventional steam reforming.

Steam reforming of bio-oil component with chemical formula $C_nH_{m}O_k$ can be represented as Eq. 2.4;

$$C_nH_{m}O_k + (n - k)H_2O \rightarrow nCO + (n + (m/2) - k)H_2$$  \hspace{1cm} (2.4)

Water gas shift reaction (WGS) constitutes an integral part of the reforming reaction which is shown below (see Eq. 2.5):

$$CO + H_2O \rightarrow CO_2 + H_2 \hspace{1cm} \Delta H^{\circ}_{298} (kJ/mol) = -41$$  \hspace{1cm} (2.5)

Considering both the reactions (Eqs. 2.4 and 2.5) occurring in stoichiometry manner as represented above the overall reaction can be denoted as follows:

$$C_nH_{m}O_k + (2n - k)H_2O \rightarrow nCO_2 + (2n + (m/2) - k)H_2$$  \hspace{1cm} (2.6)

Eq. 2.6 is an endothermic reaction and results in an increase in the number of moles of hydrogen. Le-Chatelier’s principle is followed here, wherein; high temperatures, low pressures and high water/feedstock ratios favour $H_2$ production. While $CH_4$ formation is favoured at high pressures, its yield decreases as the temperature and water/feed ratio increases. The overall reforming reactions for the selected four model bio-oil compounds (viz., acetol, propylene glycol, ethyl acetate and glyoxal) are given below (see Eqs. 2.7, 2.8, 2.9 and 2.10):

Acetol :
$$C_3H_6O_2 + 4H_2O \rightarrow 3CO_2 + 7H_2$$  \hspace{1cm} (2.7)

Propylene Glycol:
$$C_3H_8O_2 + 4H_2O \rightarrow 3CO_2 + 8H_2 \hspace{1cm} \Delta H^{\circ} 298 (kJ/mol) = 211.0$$  \hspace{1cm} (2.8)

Ethyl acetate:
$$C_4H_8O_2 + 6H_2O \rightarrow 4CO_2 + 10H_2 \hspace{1cm} \Delta H^{\circ} 298 (kJ/mol) = 320.1$$  \hspace{1cm} (2.9)
Glyoxal
\[ \text{C}_2\text{H}_2\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 3\text{H}_2 \] (2.10)

For the model compounds studied, the maximum stoichiometric yield are, acetol 2.3 mol H$_2$/mol C, propylene glycol 2.67 mol H$_2$/mol C, ethyl acetate 2.5 mol H$_2$/mol C and glyoxal 1.5 mol H$_2$/mol C. However, in reality H$_2$ yield is lower than the stoichiometric maximum because of two main undesirable products, CO and CH$_4$, which are formed via WGS and methanation reaction. Eq. 2.11 represents cracking of feedstock and interconversion of the gaseous product which can be given as:

\[ \text{C}_n\text{H}_m\text{O}_k \rightarrow \text{C}_x\text{H}_y\text{O}_z + \text{gas (CO,CO}_2, \text{CH}_4, \text{H}_2 \ldots ) + \text{coke} \] (2.11)

\[ \text{C}_n\text{H}_m\text{O}_k \rightarrow \text{C}_x\text{H}_y\text{O}_z + \text{H}_2 \] (2.12)

\[ \text{H}_2 + \text{CO}_2 \rightarrow \text{H}_2\text{O} + \text{CO} \quad \Delta H^\circ 298 (\text{kJ/mol}) = 41.4 \] (2.13)

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2 \quad \Delta H^\circ 298 (\text{kJ/mol}) = -41.4 \] (2.14)

\[ \text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \Delta H^\circ 298 (\text{kJ/mol}) = -206.2 \] (2.15)

\[ \text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta H^\circ 298 (\text{kJ/mol}) = -165.1 \] (2.16)

\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad \Delta H^\circ 298 (\text{kJ/mol}) = 206.1 \] (2.17)

\[ \text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2 \quad \Delta H^\circ 298 (\text{kJ/mol}) = 165.1 \] (2.18)

Bio-oil feedstocks are generally considered to be thermally unstable, the homogenous reactions like decomposition of bio-oil (as shown in Eq. 2.11) and dehydration of bio-oil (as shown in Eq. 2.12) may occur before the feed reaches the catalyst surface producing undesirable organic byproducts which in turn reduces hydrogen selectivity. In steam reforming process CO is an intermediate and one of the main by-products. Decomposition of organic compounds (as shown in Eq. 2.11) is also favoured by low reaction temperature which in turn results in low efficiency of steam reforming favouring CO formation. However, a high reaction temperature promotes reverse water gas shift reaction (as shown in Eq. 2.13) which also increases CO production. Conversely, water gas shift reaction (as shown in Eq. 2.14) and methanation of CO (as shown in Eq. 2.15) contributes in eliminating CO at lower temperatures as shown by Ni et al. (2007) and Ma et al. (2008).
Methane, another major by product in steam reforming reaction reduces hydrogen yield. Studies of Basagiannis and Verykios (2007, 2008) and Kechagiopoulos et al. (2007) showed decomposition of the organic molecules and methanation of carbon oxides (as represented by Eqs. 2.15 and 2.16) to be the main path for CH₄ formation while the steam reforming of methane is thermodynamically limited (as shown in Eqs. 2.17 and 2.18) further contributes in H₂ and CO₂ selectivity at high temperatures.

Wang et al. (1996) and Mackie and Doolan (1984) demonstrated bio-oil compounds as thermally unstable at typical temperatures of the reformers As a result thermal decomposition (cracking) of most oxygenates leads to coke formation. Reactions for coke formation or elimination are summarized as Eqs. 2.19-2.24.

\[
\begin{align*}
\text{CH}_4 & \rightarrow \text{C} + 2\text{H}_2 & \Delta H^\circ 298\text{ (kJ/mol)} = -74.9 \\
2\text{CO} & \rightarrow \text{C} + \text{CO}_2 & \Delta H^\circ 298\text{ (kJ/mol)} = -172.4 \\
\text{CO} + \text{H}_2 & \rightarrow \text{C} + \text{H}_2\text{O} & \Delta H^\circ 298\text{ (kJ/mol)} = -131.3 \\
\text{CO}_2 + 2\text{H}_2 & \rightarrow 2\text{H}_2\text{O} + \text{C} & \Delta H^\circ 298\text{ (kJ/mol)} = -90.1 \\
\text{C} + \text{H}_2\text{O} & \rightarrow \text{CO} + \text{H}_2 & \Delta H^\circ 298\text{ (kJ/mol)} = 131.3 \\
\text{C} + \text{CO}_2 & \rightarrow 2\text{CO} & \Delta H^\circ 298\text{ (kJ/mol)} = 172.4
\end{align*}
\]

Adhikari et al. (2007) investigated steam reforming of glycerine for hydrogen production and showed a detailed comparative thermodynamic study wherein steam reforming of hydrocarbons involves a risk of carbon deposition, which in turn reduces the effective surface area, lowers the heat-transfer rate from catalyst to gas, or plugs the void space within the catalyst. Carbon deposition may arise because of the decomposition of organics (as shown in Eq. 2.11), CH₄ (as shown in Eq. 2.19) and disproportion of CO (as shown in Eq. 2.20). Also, CO and CO₂ react with H₂ (as shown in Eqs. 2.21 and 2.22) resulting in coke formation. Coke formation can be eliminated under certain conditions in presence of steam (see Eq. 2.23) and in presence of carbon dioxide (see Eq. 2.24). The heat of reactions represented by Eqs. 2.5, 2.8, 2.9, 2.13-2.18 and 2.19-2.24 at 298 K are reported by Hu and Lu (2009).

Thus, there are numerous routes for bio-oil feedstocks conversion. Nevertheless, the main reaction mechanism can be only formulated by the comprehensive study of properties of a feedstock and the experimental parameters.
(such as reaction temperature, reaction pressure, catalyst and S/C of feedstock) which are discussed in chapters 5-10

2.2 Thermodynamic analysis

Steam reforming of bio-oil for hydrogen production involves complex reactions. As a result, several intermediate by-products are formed which end up in the product stream affecting the final purity of the hydrogen produced. Furthermore, the yield of hydrogen depends upon several process variables, such as system pressure, temperature, volumetric flow rate and ratio of reactants. The first step to understand the effects of the aforementioned variables is a complete thermodynamic analysis. There are a few studies on the thermodynamic aspects of bio-oil reforming processes available. Vagia and Lemonidou (2007) and Xiea et al. (2011) presented a comprehensive insight into thermodynamics of steam reforming of model bio-oil compounds. Vagia and Lemonidou (2007) discussed that composition of an exit gas stream and important process parameters affecting H₂ yield are usually predicted by the thermodynamic analysis. They performed a detailed thermodynamic analysis of H₂ production via steam reforming with ASPEN 11.1 using acetic acid, ethylene glycol, and acetone as model compounds of bio-oil. Peng-Robinson property method and Gibbs reactor were selected with equilibrium compositions being computed by the minimization of Gibb's free energy. The important specifications fed into the software included reactant and product inlet composition, inlet temperature, pressure, reaction temperature, and steam to carbon (S/C) ratio. They showed that equilibrium concentrations of ethane, ethylene, acetylene and other oxygenated compounds in the product stream were negligible. It was established that H₂ yield was favoured at increased temperatures and S/C (steam to carbon ratio) at atmospheric pressure. At optimum conditions of 900 K, atmospheric pressure and S/C=3 (steam to carbon ratio), 0.208 kmol/s of the mixture of the model compounds (acetic acid, ethylene glycol and acetone at 4:1:1 molar ratios) yielded about 1 kmol/s of hydrogen. No coke formation was reported at temperatures higher than 600 K. They also established that bio-oil can be thermally decomposed to form a mixture of gases containing CH₄, H₂, CO, CO₂ and H₂O.

Similar thermodynamic analysis was done by the same research group for H₂ production via auto-thermal reforming with the same model compounds Vagia and Lemonidou, (2008). They reported a maximum yield at 900 K but 20% lesser than the
yield obtained by the steam reforming. Aktas et al. (2009) conducted thermodynamic analysis of steam reforming using isopropyl alcohol, lactic acid and phenol as model compounds of bio-oil at temperatures from 600 K to 1200 K, S/C ratio from 4 to 9 and total pressure of 3 MPa. They study showed that H₂ yield increased with increasing temperature and S/C ratio.

2.3 Catalyst considerations

It is widely known that a catalyst accelerates the reactions in the reforming process. By now, Ni, Co, Pt, Ru and Rh based catalysts have been investigated. During catalytic reforming, feedstock is dehydrogenated and chemisorbed on the catalyst surface via carbon and/or oxygen atoms which depends on whether bond cleavage occurs between two carbon atoms or between a carbon and an oxygen atom. Steam reforming of bio-oils is usually carried out in the presence of a catalyst which not only increases the reaction rate but also helps achieving equilibrium faster. Catalytic reforming of bio-oils has been studied by Wang et al. (1996, 1997 and 1998), Marquevick et al. (1999), Garcia et al. (2000) and Czernik et al. (2002).

Dumesic et al. (2004) investigated aqueous phase reforming where he showed C-C bond cleavage and subsequent dehydrogenation results in the formation of adsorbed CO. The CO may either desorbs, water-gas shift or undergo methanation CH₄ may undergo decomposition, steam reforming or dry reforming while C-O bond cleavage and subsequent hydrogenation results in the formation of smaller alcohols, aldehydes, ketones. Rearrangement of atoms and dehydrogenation may occur, thereby producing alkenes and carboxylic acids.

Thus during catalytic steam reforming of bio-oil C-C bond cleavage is desired as it facilitates formation of H₂ while C-O bond cleavage results in formation of more liquid byproducts.

Galdamez et al. (2005) prepared Ni-Al catalysts by co-precipitation and studied the extent to which loading of La₂O₃ on Ni-Al catalyst affected the hydrogen yield while, they also conducted non-catalytic steam reforming and confirmed that the H₂, CO₂ yields were low in the absence of catalyst. Galdamez et al. (2005) also noticed that the total gas yield decreased when catalyst weight is reduced. Galdamez et al. (2005) reduced Ni-Al catalyst with a mixture of H₂ and N₂ gas for 1 h at 923 K. Czernik et al. (2002) and Kechagiopoulos et al. (2006) used nickel-based naphtha reforming catalyst to produce hydrogen. Kechagiopoulos et al. (2006) used C11-NK
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catalyst which has higher potassium content compared to other Ni catalysts. The higher potassium content plays a vital role in inhibiting coke formation and a 90% hydrogen yield was reported for the equi-molar mixture of model compounds. Pan et al. (2006) employed C12A7-Mg catalyst and determined its lifetime to be about 210 min at 1023 K. Steam reforming of bio-oil at 1023 K using this catalyst resulted in a hydrogen yield of 80%. Wang et al. (2007) conducted reforming over three catalysts: C12A7/15% Mg, 12% Ni/γ-Al2O3, and 1% Pt/γ-Al2O3 at 923 K and the observed hydrogen yields were 56.7%, 58.1%, and 66.8%, respectively. Yan et al. (2010) reformed bio-oil with commercial Z417 catalyst along with CO2 sequestration using calcined dolomite and reported a hydrogen yield of about 75%. Lin et al. (2010) performed catalytic reforming of bio-oil over Co-Zn-Al catalyst electrochemically by passing ac current in a Ni-Cr wire tangled around the catalytic column.

2.4 Steam reforming of Bio-oil, aqueous bio-oil and model bio-oil compounds

Czernik et al. (2007) investigation shows steam reforming of whole bio-oil at 1123 K; steam to carbon ratio (S/C) was 5.8 and space velocity of 920 h⁻¹ in fluidized bed reactor over commercial C11-NK and NREL#20 catalyst. H2 yield was found as 70–80%. Wang et al. (2007) performed steam reforming of whole bio-oil in a fixed bed micro-reactor at a temperature of 473-1023 K, steam to carbon ratio (S/C) of 1.5-9, GHSV of 10,000 h⁻¹. They used a wide range of catalyst C12A7, C12A7 doped with 18% Mg, C12A7 doped with 25% K, C12A7 doped with 12% Ce, C12A7 doped with 12% Mg, Al2O3 doped with 12% Mg, Al2O3 doped with 18% Mg. Maximum H2 yield of 80% and carbon conversion of 96% was achieved at 1023 K, steam to carbon ratio (S/C) > 4, GHSV of 10,000 h⁻¹ and C12A718% Mg catalyst. Also, they studied steam reforming of volatile organic components of crude bio-oil in a fixed bed reactor at 1023 K, steam-to-carbon (S/C) of 6 and GHSV equal to 26,000 h⁻¹ over C12A7 doped with 15% Mg, 12% Ni/γ-Al2O3 and 1% Pt/γ-Al2O3 catalysts. C12A7/15% Mg exhibited high reforming activity, a H2 yield of 71% and carbon conversion of 93 % was determined.

Steam reforming of aqueous fraction of bio-oil in a bench scale fixed bed reactor was conducted over a temperature range of 773-973 K; water to bio-oil ratio was 1:1. Catalyst used in this study Yan et al. (2010) was commercial catalyst Z417. Optimum temperature with CO2 capture was 823-923 K; their investigation suggested that use of dolomite capture CO2 and in turns enhances H2 yield. Maximum H2 yield
was 75% at 873 K. A study by Medrano et al. (2010) utilized Ni/Al₂O₃ catalyst modified with Mg and Ca in a fluidized bed at 823 K and GHSV of 11,800 h⁻¹. Coke formation was reduced by decreased space velocity and increased O₂. Mg modified catalyst performed better than Ca modified catalyst. Hydrogen yield of 0.1056 g/g of organics was reported for Mg modified catalyst. Basagiannis and Verykios (2007) worked on steam reforming of acetic acid and aqueous fraction of bio-oil over 5% Ru/MgO/Al₂O₃ in a fluidized bed reactor at 1073 K, steam to carbon ratio (S/C) equal to 5.58, liquid feeding rate was 1.84-2.94 g/min. They found that MgO was efficient in converting CO to CO₂ and enhancing steam adsorption capacity of the catalyst. The selectivity of H₂ in the form of pellets was the highest and was close to 100%. Kechagiopoulos et al. (2006) used Ni based catalyst in a fixed bed at 873-1173 K, steam to carbon ratio (S/C) in a range of 2-8.2 and GHSV equal to 300-500 h⁻¹ for steam reforming of acetic acid, acetone, ethylene and aqueous fraction of bio-oil. It was found that high potassium content in the catalyst inhibits coke formation. At T > 873 K, H₂ yield was determined as 60% for aqueous fraction bio-oil while in case of model compounds reforming H₂ was yield 90%. Yan et al. (2010) used Ni/Co₂-ZrO₂ catalyst, in fixed bed reactor at a temperature range of 723-1073 K, water to aqueous fraction of bio-oil ratio was 4.9 and Ni loading was 12% while Ce loading was 7.5%. It was observed that conversion of aqueous fraction bio-oil was 69.7% higher than that of commercial Z417 catalyst. Bimbela et al. (2011) showed steam reforming of acetic acid, acetol, butanol and aqueous fraction of bio-oil over 33 % Ni and 28% Ni based catalyst at 923 K, steam-to-carbon ratio (S/C) was 5.58-14.71, GHSV ranges from 4789- 19,000 h⁻¹. Their study concluded that catalytic steam reforming of aqueous fraction of bio-oil at 923 K, steam-to-carbon ratio (S/C) 7.6 favours H₂ production while in case of non catalytic it produces gas with LHV= 17 MJ/STP m³, but energy efficiency of process is low.

Steam reforming of model compounds of bio-oil: Knowledge on the reforming reaction pathway is essential for process development. There are several studies on the steam reforming of bio-oil and its aqueous fraction available. (Basagiannis and Verykios, 2007; Czernik et al., 2002, 2005; Garcia et al., 2000; Kechagiopoulos et al., 2006, 2009; Ortiz-Toral et al., 2011; Palmeri et al., 2008, Seyedeyn-Azad et al., 2011; Wang et al., 1997, 1998). The chemical composition of the bio-oil aqueous fraction is complex; thus, a complete chemical analysis for all constituents is difficult. Therefore, model compound studies that elucidate the behaviour of a compound and its
interaction with others are useful. By now, the reforming reactions of methanol have been deeply studied by (Conant et al., 2008; Fukuhara et al., 2008; Makarshin et al., 2007; Papavasiliou et al., 2007). Ethanol reforming was conducted by (Byrd et al., 2007; Campos-Skrobot et al., 2008; Morgenstern et al., 2005; Wang et al., 2002). Ethylene glycol reforming was in-depth analyzed by (Dauenhauer et al., 2006; Davda et al., 2005; Kechagiopoulos et al., 2007; Shabaker et al., 2005). Steam reforming of glycerol was reported by (Douette et al., 2007; Slinn et al., 2008; Adhikari et al., 2007; Sutar et al., 2010). There are many studies on acetic acid reforming; some of them are (Basagiannis and Verykios, 2006, 2007; Hu and Lu, 2006, 2007, 2008; Guell et al., 2008; Iulianelli et al., 2008; Takanabe et al., 2006; Vagia et al., 2007). Steam reforming of phenol was investigated by Adjaye et al. (2002), Rioche et al. (2005), and Wang et al. (1997). Acetone reforming was examined by Kechagiopoulos et al. (2006), Rioche et al. (2005) and Vagia et al. (2007). Besides, H\textsubscript{2} production from a series of model compounds derived from bio-oil was considered in Hu and Lu (2009) and Marquevich et al. (1999). A detailed comparison of different studies in reforming of bio-oil has been discussed in Table 2.1.

2.5 Other reforming methods

Vagia and Lemonidou (2008) performed thermodynamic analysis of auto-thermal reforming of selected components of aqueous bio-oil fraction to determine the optimum amount of oxygen required to carry out an energy neutral process. They studied the effect of temperature and pressure on H\textsubscript{2} production. They reported that at optimum operating conditions, i.e, 900 K, 1 kmol of H\textsubscript{2} is produced from 0.245 kmol of bio-oil, which is 20% lower than the H\textsubscript{2} yield obtained by steam reforming method.

Marda et al. (2009) conducted non-catalytic partial oxidation of whole bio-oil in a tubular reactor at 898-1123 K, O\textsubscript{2}: C ratio was 1.4-1.6. H\textsubscript{2} yield was determined as 25%. Rennard et al. (2008) performed auto-thermal catalytic partial oxidation of bio-oil using esters and acids as model compounds over platinum and rhodium based catalysts. Marda et al. (2009) reported a low H\textsubscript{2} yield of about 25% while Rennard et al. (2008) have concentrated on synthesis gas production.

Aqueous phase reforming process model bio-oil compounds was developed by Dumesic et al. (2002) which was conducted at high pressure (at around 60 bar) and low temperature (at around 543 K). This process reduces CO content in product gas and since reaction occurs at low temperature energy required to convert liquid
reactant to vapour is also saved. Catalysts prepared from a variety of metal precursors displayed similar activity and H₂ selectivity, the H₂ production rates were influenced by the type of support. Besides, the catalyst performance was affected by metal loading and metal particle size, too. Iriondo et al. (2008) used different promoters and found that Ni catalyst does not work very well for glycerol due to severe deactivation. Glycerol steam reforming over a Ni/Al₂O₃ catalyst modified with Ce, La, Mg, and Zr. They found that these promoters facilitated H₂ production. While Mg enhanced surface Ni concentration and Zr facilitated steam activation, Ce and La promoted catalyst stability. The aqueous phase reforming reaction was studied, too, and it was found that glycerol conversion in the presence of Ce, La, and Zr was higher.

2.6 Conclusions

Although four types of bio-oil reforming processes – steam, aqueous, partial oxidation and auto-thermal – have primarily been investigated, steam reforming reaction of bio-oil has received considerable attention. Thermodynamic analyses suggest that the reaction pathways are complex. Very few studies on the influences of promoters, metal loading, metal particle size and method of catalyst preparation on bio-oil reforming have been published. Besides, the influences of reaction temperature, pressure, water-to-bio-oil ratio and the presence of contaminants in the feed on H₂ production have been reported. By now, the information on the reaction mechanism and kinetics of steam reforming of bio-oil and their model compounds is missing in the open literature. Also, there exists scope for finding an efficient catalyst for H₂ production from bio-oil. It has been found that Ni facilitates H₂ production from bio-oil but undergoes coking, hence the catalyst are modified over different supports or catalyst is doped with other metal content in order to inhibit coke formation. Also, the major concerns of the process are by-product formation (e.g. CH₄, CO), catalyst deactivation and high energy consumption. Thereby, a comprehensive study on kinetics and reaction mechanism is desirable.
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<th>Catalyst</th>
<th>Reaction Conditions</th>
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<th>Reference &amp; Research Highlights</th>
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</table>
| Ni-Al promoted with La           | Reactor: fluidized bed  
T: 723-973 K  
S/C: 5.58  
Liquid feeding rate: 1.84-2.94 g/min | Acetic acid | Galdamez et al. (2005)  
Presence of catalyst showed increase in H₂ yield. No effect on H₂ yield for La promoted Ni-Al catalyst. At 923 K, 1.84 g/min acetic acid feeding rate H₂ yield: 0.029 g/g |
| Ni, Rh or Ir supported on calcium aluminates | Reactor: fixed bed quartz reactor  
T: 823-723 K, S/C: 3, Space velocity= 30,000 h⁻¹ | Acetic acid | Vagia et al. (2008)  
Coke deposition over Ni loaded catalyst was higher than that with the Rh or Ir. H₂ yield Ni/CaO.2Al₂O₃ > Ir/CaO.2Al₂O₃ >Rh/CaO.2Al₂O₃  
H₂ yield for acetone =70% at 750°C |
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<th>Catalyst</th>
<th>Reactor: fluidized bed</th>
<th>Temperature (K)</th>
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<td>5% Ru/MgO/Al₂O₃</td>
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<td>1073</td>
<td>5.58</td>
<td>1.84-2.94</td>
<td>Acetic acid, Aqueous fraction of bio-oil</td>
<td>Basagiannis and Verykios (2007) Role of MgO is vital in converting CO to CO₂ and enhancing steam adsorption capacity of the catalyst. The selectivity of H₂ in the form of pellets was the highest and was close to 100%</td>
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<td>33% Ni and 28% Ni based catalyst</td>
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<td>923</td>
<td>5.58-14.71</td>
<td>4789-19,000</td>
<td>Acetic acid, Acetol, Butanol, Aq. fraction of bio-oil</td>
<td>Bimbela et al. (2011) Catalytic steam reforming of aq. fraction of bio-oil at 923 K and S/C ratio 7.6 favours H₂ production while in case of non catalytic it produces gas with LHV= 17 MJ/STP m³, but energy efficiency of process is low.</td>
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<td>Ni/Al₂O₃</td>
<td></td>
<td>473-873</td>
<td>6 mol/mol</td>
<td></td>
<td>Methanol, Ethanol, 1-propanol, Butanol, 2-propanol, 1,2-propanediol, Glycerol, Propionaldehyde, Acetone and Propionic acid</td>
<td>Hu and Lu (2009) Alcohol steam reforming favors byproducts like CH₄ and coke. H₂ selectivity increases with increase in hydroxyl group. aldehyde (propionaldehyde) steam re-forming produced less of CH₄ and other organic byproducts. acetone showed a high tendency for polymerization to coke.</td>
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</table>
### Literature Review

<table>
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<th>Catalyst</th>
<th>Reactor</th>
<th>Temperature</th>
<th>S/C Ratio</th>
<th>Feedstock Compounds</th>
<th>Authors</th>
<th>Description</th>
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</thead>
</table>
| Ni/Al₂O₃ | T: 973 K  
S/C ratio: 6 mol/mol | Acetic acid,  
Ethyl acetate,  
Ethylene glycol,  
Acetone,  
m-xylene,  
Glucose | Hu and Lu (2009) | High temperature and S/C favors feedstock conversion and removal of the by-products. Coke formation rates in order: glucose ~ m-xylene > acetone > ethyl acetate > ethylene glycol > acetic acid. Coke formation in glucose, m-xylene, and acetone reforming due to decomposition or polymerization of feedstock, while in case of ethyl acetate, ethylene glycol, and acetic acid reforming by-products such as C₂H₄, CO, or acetone were the reason for coke formation. |
| Ni based catalyst | Reactor: fixed bed  
T: 873-1173 K  
S/C: 2-8.2  
GHSV: 300-500 h⁻¹ | Acetic acid  
Acetone  
Ethylene glycol  
Aqueous fraction of bio-oil | Kechagiopoulos et al. (2006) | High potassium content in the catalyst inhibits coke formation. T > 873 K aq. fraction of bio-oil: H₂ yield 60%; model compounds reforming 90% H₂ yield |
| Ni-Al, Ni-Al promoted Ca and Co | T: 873-923 K  
S/C ratio: 4.6 mol/mol | Acetol | Garcia et al. (2007) | H₂ and CO₂ yield increases with increase in temperature and S/C ratio. Feedstock conversion was observed as 87.22% while H₂ yield 0.13 mol/mol. |
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temperature</th>
<th>S/C Ratio</th>
<th>Product</th>
<th>Reference</th>
<th>Notes</th>
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</thead>
<tbody>
<tr>
<td>Ni-Al modified by Mg and Ca</td>
<td>T: 923 K S/C ratio: 5.58 mol/mol</td>
<td>Acetol</td>
<td>Increase in W/F ratio and temperature favours H₂ yield. Feedstock conversion = 94.57 % while H₂ yield 0.13 mol/mol.</td>
<td>Medrano et al. (2009)</td>
<td></td>
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<tr>
<td>Ni-Al</td>
<td>T: 823 K T: 923 K T: 1023 K S/C ratio: 5.58 mol/mol</td>
<td>Acetol</td>
<td>Severe coke formation at 923 K in 2h, At T= 550°C, 650°C and 750°C feedstock conversion = 38.15%, 91.53% and 97.83% while H₂ yield 0.06 mol/mol, 0.16 mol/mol, and 0.17 mol/mol respectively.</td>
<td>Bimbela et al. (2009)</td>
<td></td>
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