Review

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Hydrothermal conversion of glycerol to chemicals and hydrogen: review and perspective

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Abstract: As biodiesel production worldwide is expanding dramatically, its main by-product glycerol (accounting for 10 wt% of total products) should find other applications by converting it to value-added products. Hydrothermal process is used in the conversion of glycerol to acrolein, lactic acid, and other promising commodity chemicals. This review mainly focuses on the hydrothermal conversion of glycerol to chemicals in sub- and super-critical water with acid /base catalysts or without catalysts. Hydrothermal gasification of glycerol to hydrogen is also covered. Furthermore, the mechanisms of hydrothermal conversion of glycerol under different conditions are introduced. The problems and future perspective for the practical applications of glycerol are also discussed. © 2012 Society of Chemical Industry and John Wiley & Sons Ltd

Keywords: glycerol; hydrothermal; acrolein; lactic acid; hydrogen; supercritical water

Introduction

Because of limited resources of fossil fuels and rising energy demand, as well as global warming, it is imperative to develop alternative fuels.[1] Biodiesel derived from plant oils or animal fats has great potential as an alternative diesel fuel. It can be employed in current diesel engines either blended with fossil diesel or in pure form.[2–4] In general, biodiesel is produced by the transesterification of plant oils with homogeneous or heterogeneous acid or base catalysts.[5,6] World biodiesel production reached 11.1 million tons in 2008, and is expected to double by 2012.[7] Production of 1 ton biodiesel will produce about 0.1 ton of glycerol as a main by-product according to the general reaction in Fig. 1. The United States claimed

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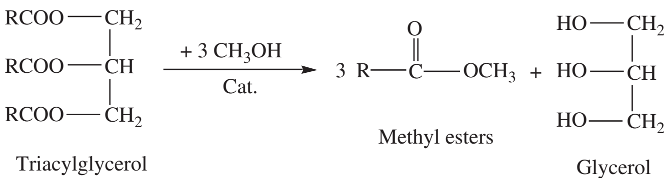

Figure 1. The transesterification reaction of vegetable oils to yield biodiesel and glycerol.

that 2% of on-road diesel would be replaced with biodiesel in a B2 policy (2% biodiesel, 98% fossil diesel) by 2012, which means that more than 360 million kg glycerol could be produced.[8] In March 2007, as part of the Climate Change and Energy Package, the European Council adopted a 10% binding target for biofuel consumption to be reached by 2020.[9] If this target is achieved, millions of tons of glycerol will be produced.

Since crude glycerol generated from conventional biodiesel processes contains impurities such as water, alcohol, salts, and traces of fatty acids, it should be purified further for traditional applications.[10] Refined glycerol is widely used in food (11%), pharmaceuticals (18%), cosmetics (16%), tobacco (6%), and other industries depending on its different refining purities.[11] Although high purified glycerol has versatile applications, the refinery processing is extremely expensive, partially resulting in the proportion of refined glycerol steadily decreasing.[12] With the increased production of biodiesel, excessive glycerol is produced that leads to its market price falling sharply. New applications of glycerol should be developed to substantially increase the demand and price of glycerol, and to make biodiesel production more profitable and sustainable.[11] Therefore, conversion of glycerol to other value-added products is becoming increasingly important and receiving a great deal of attention. Previous studies and efforts on catalytic conversion of glycerol have been described extensively.[13–16] A variety of valuable chemicals and biofuels can be produced from glycerol by selective catalytic processes including oxidation, dehydration, hydrogenolysis, etherification, esterification, gasification, carboxylation, and biological transformations.

Hydrothermal process carried out in subcritical water (< critical point of water (CP): 647 K, 22.1 MPa) or supercritical water (SCW > CP) is an effective and attractive thermochemical method for the conversion of biomass (e.g. carbohydrates, lignocellulose, lipids, and protein derivatives) to a variety of liquid and gaseous biofuels and renewable chemicals.[17–22] Compared to biological conversion with typical drawbacks (e.g. difficult control of production conditions, complex separation steps, and low productive efficiency),[23] hydrothermal technology exhibits great potential for practical applications because of its high throughput, high energy efficiency, easy separation, and excellent miscibility.[24,25]

Hydrothermal water, i.e. subcritical and supercritical water, possesses many unique features serving as solvent, reaction medium, reactant, and catalyst in reactions.[26–30] In hydrothermal chemical reactions, the physical and chemical properties of water show dependencies on the temperature-pressure regime, particularly on temperature.[31] Figure 2 gives selected properties of water as a function of temperature at 24 MPa.[32] First, hydrothermal water exhibits good solubility to organics or gases as many non-polar organic solvents because of its low dielectric constant (ε) which drops from a value of about 80 at ambient conditions to 5 above the critical temperature at 24 MPa (Fig. 2, curve 1).[33] This makes organics react in a homogeneous phase. Secondly, hydrothermal water can promote catalytic conversion of biomass effectively without adding any acid or base due to the high concentration of its ionic product $\{K_w = [H^+]\bullet[OH^-]; [H^+] = [OH^-]\}$ that increases with temperature and reaches the maximum at around 573 K (24 MPa), and then decreases sharply as temperature rises further to SCW region (Fig. 2, curve 3). Therefore, hydrothermal water can perform as a weak-polar solvent (low ε) as well as an acid/base catalyst (high K_w).[34] Thirdly, the high diffusion rate and

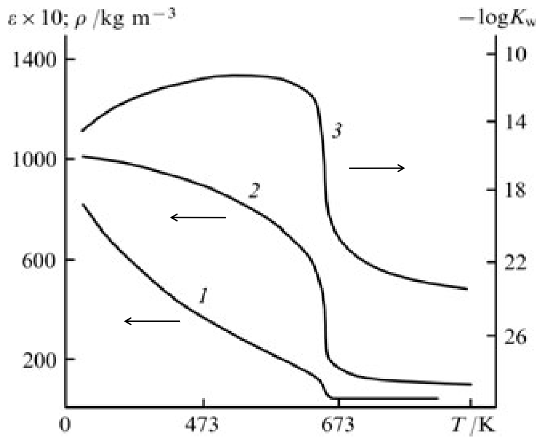

Figure 2. Selected properties of (1) dielectric constant (ε), (2) density (ρ), and (3) ionic product (K_w) of water as a function of temperature at 24 MPa. Reproduced with permission.[32] © 2005 Russian Academy of Sciences and Turpion Ltd.

low viscosity of hydrothermal water resulting in efficient heat transfer and rapid mass diffusion, will make reactions fast, especially in heterogeneous catalytic reaction systems.[35]

These properties of water vary with temperature and pressure (or density) over wide ranges under subcritical and supercritical conditions. Consequently, a hydrothermal medium can support ionic, polar non-ionic, and free-radical reactions in a homogeneous phase. Due to the relatively high density and high ionic product of subcritical water, ionic reactions such as dehydration of carbohydrates and alcohols, are accelerated.[36,37] Whereas free-radical reactions dominate at high temperature, and lower density conditions in SCW result in gasification.[38,39] However, no review paper that systematically introduces hydrothermal conversion of glycerol to chemicals and biofuels has been reported up to now. Therefore, in this paper, selective hydrothermal conversion of glycerol in subcritical and supercritical water is introduced and reviewed. Value-added products, including acrolein, lactic acid, and hydrogen, are produced. New ways and future perspectives for hydrothermal processing of glycerol for industrial applications are discussed and proposed.

Non-catalytic hydrothermal conversion

Hydrothermal degradation of glycerol strongly depends on the properties of water under subcritical and supercritical conditions. Different products are produced under different conditions via different processes. Table 1 gives some results of non-catalytic hydrothermal conversion rate of glycerol (e.g. 6–99%) in flow (16–98 s) and batch (e.g. 60 min) reactors.

Degradation mechanism

Antal *et al.*[28] and Westacott *et al.*[40] proposed that ionic reactions were favored when $K_w > 10^{-14}$, and free-radical reactions were favored when $K_w < 10^{-14}$, which provided a potential direction for glycerol decomposition in subcritical and supercritical water. Antal *et al.*[41] also found that heterolytic acid-catalyzed carbonium ion mechanism resulted in the formation of acrolein by the elimination of water from glycerol at lower temperatures, whereas homolytic cleavage of C-C bonds led to the preferential formation of acetaldehyde at higher temperatures. The specific mechanism could be controlled by both temperature and pressure. The non-Arrhenius behavior of the overall degradation, reaction rate, and product distribution showed that major two reaction pathways occurred: ionic and free radical reactions.[42] The kinetic model of the degradation of glycerol is proposed according to the occurrence of two competing reaction pathways in Fig. 3: (a) ionic reaction steps, which are preferred at higher pressures and/or lower temperatures, and (b) a free radical degradation which dominates at lower pressures and/or higher temperatures. The model also indicated that glycerol dehydration into acrolein mainly

Table 1. Typical results of non-catalytic or acid-catalytic dehydration of glycerol in hydrothermal water.

Catalyst	T (K)	P (MPa)	Reactor type	Reaction time	C (%)	S (%)	Y (%)	Ref.
None	573	34.5	Flow	16 s	6	–	–	[41]
None	740	45	Flow	98 s	31	6.6	–	[42]
None	573	30	Batch	60 min	99	–	0.2	[43]
H_2SO_4	463	0.1	Batch	–	–	–	49	[48]
H_2SO_4	623	34.5	Flow	19 s	39	100	39	[41]
H_2SO_4	623	34.5	Batch	25 s	55	86	47.3	[49]
H_2SO_4	523	34.5	Batch	–	1	–	–	[50]
H_2SO_4	673	34.5	Flow	10 s	92	81	74	[51]
$ZnSO_4$	633	25	Flow	60 s	50	75	37.5	[52]
$ZnSO_4$	633	34	Flow	60 s	62	59	37	[53]
H_3PO_4/Clay	573	0.1	Batch	–	–	–	72.3	[54]
$H_3PO_4/\alpha\text{-}Al_2O_3$	573	0.1	Batch	–	–	–	75	[55]
HY	523	7	Batch	10 h	89	99.5	88.5	[56]

T: reaction temperature; P: reaction pressure; C(%): glycerol conversion rate = (moles of glycerol converted/total moles of initial glycerol) × 100; S (%): acrolein selectivity = (moles of acrolein formed/moles of glycerol converted) × 100; Y(%): acrolein yield = (moles of acrolein formed/total moles of initial glycerol) × 100.

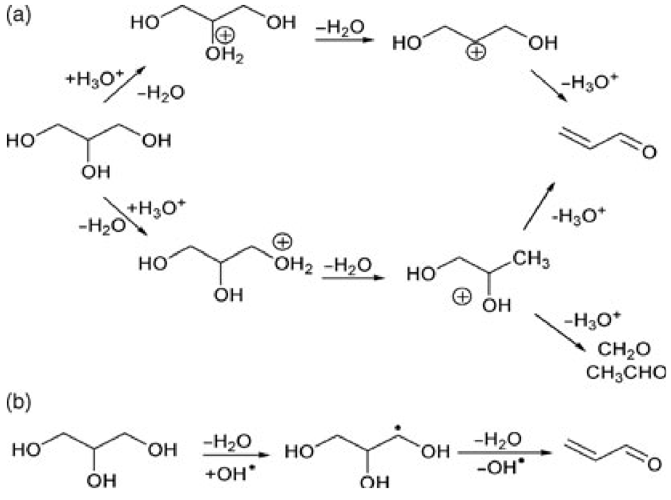

Figure 3. Reaction pathways for the hydrothermal degradation of glycerol: (a) an ionic reaction, and (b) a free radical reaction.[42]

proceeded through ionic reactions, whereas allyl alcohol was formed through radical reactions and then fragmented into acetaldehyde and formaldehyde via bond scission reaction.[39,42] Generally, non-catalytic hydrothermolysis of glycerol occurs via both ionic and free-radical mechanisms simultaneously, and thus, many chemical products, such as acrolein, acetaldehyde, formaldehyde and allyl alcohol, are formed.

Degradation reactions

In 1985, Antal *et al.*[41] examined the decomposition of glycerol in SCW. Acrolein, acetaldehyde and other products were obtained. Bühler *et al.*[42] and Qadariyah *et al.*[43] studied the degradation of glycerol in subcritical and supercritical water in flow and batch reactors, respectively. Many products, such as methanol, acetaldehyde, propionaldehyde, acrolein, allyl alcohol, ethanol, formaldehyde, carbon monoxide, carbon dioxide and hydrogen, were observed.[42] However, the glycerol conversion rate was low (31 mol%). High conversion rate (99 mol%) was achieved by Qadariyah *et al.*,[43] who studied the degradation of glycerol using batch process under 573 K, 30 MPa and a reaction time of 60 min. Acetaldehyde was formed only in subcritical water and allyl alcohol only in SCW, while acrolein was formed in both regions. Apparently, a much higher glycerol conversion rate (e.g. 99%) can be achieved even at relatively low temperature (e.g. 573 K) but long reaction time (60 min) that can be conducted in batch reactors as compared with only 31% conversion rate at 740 K for 98 s in a flow reactor (Table 1).

Although non-catalytic hydrothermal decomposition of glycerol can reach a high conversion rate to many products, selectivity of products is very low (for instance, the selectivity of acrolein is only 6.6%).[42] Addition of catalysts can substantially increase the yield and selectivity of desirable products under less severe conditions (e.g. low temperature and short reaction time). Catalytic hydrothermal conversion of glycerol is introduced in the next sections.

Hydrothermal conversion with acid catalysts

There are many studies on the dehydration of glycerol to acrolein, which is an important chemical intermediate. Addition of an acid catalyst is always necessary to increase acrolein yield and selectivity. Homogeneous or heterogeneous catalyst is used to promote the reactions. Typical results of acid-catalytic dehydration of glycerol in hydrothermal water are summarized in Table 1. When acid catalysts were added, acrolein yield was substantially increased from 0.2% to 37–88.5%.

Mechanism of acrolein formation

Nimlos *et al.*[44] investigated the dehydration of neutral and protonated glycerol by using quantum mechanical calculations. The results indicated that dehydration process only occurred at relatively high temperatures. As introduced above, glycerol dehydration into acrolein mainly proceeded through ionic reactions, and thus, addition of an acid catalyst would decrease dehydration temperature substantially by increasing the concentration of ionic product. Tsukuda *et al.*[45] and Chai *et al.*[46] proposed a formal reaction network (Fig. 4): First, glycerol was dehydrated to two intermediate enols, which were in tautomeric equilibrium with the corresponding ketone (hydroxyacetone) and aldehyde (hydroxypropionaldehyde). Then, hydroxypropionaldehyde was dehydrated further to acrolein or fragmented to acetaldehyde and formaldehyde via retroaldol reaction. Tsukuda *et al.*[45] confirmed that the key to obtaining high acrolein selectivity lies in the control of the first dehydration step, whereby the formation of hydroxypropionaldehyde must be favored over the formation of hydroxyacetone, which is the main byproduct of the process.

Although adding an acid catalyst enhanced the yield of acrolein, the strength of the acid catalyst must be carefully

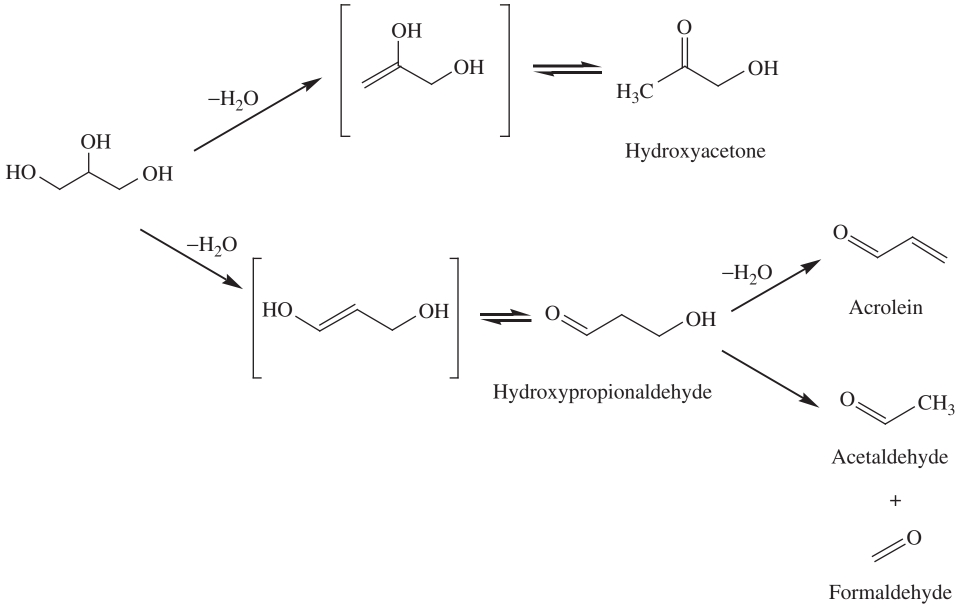

Figure 4. Reaction pathway for the conversion of glycerol to acrolein.[45,46]

controlled because of weak acidity giving low selectivity, whereas strong acidity results in accelerated deactivation.[46] In addition, the type of acid, such as Brønsted or Lewis acid, has an important influence on catalytic performance. Alhanash *et al.*[47] found that Lewis acid catalysts need high temperatures to be activated due to the high activation energy as compared with Brønsted acid catalysts. And Lewis acid catalysts have high selectivity for hydroxyacetone.

In the following sections, glycerol dehydration is discussed further in homogeneous and heterogeneous catalytic systems.

Homogeneously-catalyzed dehydration

In the homogeneously-catalyzed dehydration of glycerol, strong homogeneous inorganic acid (e.g. sulfuric acid) is always used. As early as 1936, Groll and Hearne[48] studied the dehydration of glycerol in the presence of sulfuric acid at 463 K. The yield of acrolein was nearly 50%. Ramayya *et al.*[49] studied the acid-catalyzed dehydration of glycerol in a batch reactor near the critical point of water, and 55% glycerol conversion rate and 86% acrolein selectivity were achieved under hydrothermal conditions of 623 K, 34.5 MPa and reaction time 25 s with 5 mM sulfuric acid. Antal *et al.*[50] converted 0.1 M glycerol with 0.01 M sulfuric acid at 523 K and 34.5 MPa but only 1% glycerol conversion rate was obtained without the formation of acrolein. Wanatabe *et al.*[51] conducted the dehydration of glycerol in hydrothermal water (573–673 K and 25–34.5 MPa) using both batch and flow reactors with sulfuric acid. Acrolein yield was enhanced by higher glycerol and H_2SO_4 concentrations, and higher pressure. Approximate 80% selectivity of acrolein and 90% glycerol conversion rate were obtained with 5 mM sulfuric acid at 673 K and 34.5 MPa. They also found that the rate constant of acrolein formation overcame that of acrolein decomposition by adding acid under supercritical conditions. From these studies, we can conclude that a higher reaction temperature and pressure as well as a higher H_2SO_4 concentration facilitate the dehydration of glycerol to acrolein.

Glycerol dehydration in a high-pressure plug flow reactor with zinc sulfate as catalyst was studied at 573–663 K and 25–34 MPa for 10–60 s residence time.[52] It was found that increasing the amount of salt enhanced glycerol conversion rate near the critical temperature due to the decrease in activation energy. The maximum acrolein selectivity reached 75 mol% in the presence of zinc sulfate (470 ppm) at 633 K and 25 MPa, with 50% conversion rate of glycerol. Most importantly, zinc sulfate exhibits as a promising acidic catalyst for glycerol dehydration because it is less corrosive than homogeneous inorganic acids under hydrothermal conditions. Later, Lehr *et al.*[53] studied the catalytic dehydration of biomass-derived polyols including glycerol in subcritical and supercritical water. They achieved 59% glycerol conversion rate and 60% acrolein selectivity in the presence of zinc sulfate (791 ppm) at 633 K and 34 MPa.

Even though homogeneous acids or salts are more effective in promoting glycerol dehydration because of homogeneous reaction conditions, they will corrode reactors to a certain extent under hydrothermal conditions. Besides, they are very difficult to separate from reaction mixtures for reuse. So, heterogeneous catalysts with efficient activity, high selectivity, long catalyst life, and simplicity in recovery and reuse are required to catalyze the conversion of glycerol to acrolein.

Heterogeneously-catalyzed dehydration

In 1951, Hoyt and Manninen[54] patented a method to dehydrate glycerol to acrolein with 72.3% yield at 573 K using H_3PO_4 supported clay as catalyst. In the work of Neher *et al.*,[55] glycerol dehydration over various heterogeneous catalysts (e.g. zeolites, metal oxides, Nafion composites and (mixed) oxides supported inorganic acids or heteropolyacids) was studied. Glycerol (10–40 wt%) was converted with an 8–25% rate at 453–613 K over the heterogeneous catalysts with an Hammet acidity less than +2. Oliveira *et al.*[56] converted glycerol to acrolein over molecular sieves catalysts, and found that the structure and the acidity of the catalysts governed the selectivity to acrolein and hydroxyacetone. The activity had almost the same order as its acidity: HY > Hβ > Mor > SBA-15 > ZSM-23. For example, HY showed the highest activity with conversion rate of 89% and selectivity of 99.5% at 523 K and 7 MPa. They also modified the most acidic and active catalysts by Pt incorporation; however, no enhancement of conversion was obtained. As compared with many works on homogeneous catalysts, fewer studies focus on heterogeneous catalysts because of their hard contact with reactants, severe deactivation and leachability under hydrothermal conditions. Thus, stable and active heterogeneous catalysts need to be developed, and the reactor system should be specially designed for a good mixture of catalysts and reactants.

Regarding supported-catalysts, in addition to their acidities, the influences of the supports must be taken into account, such as the dispersion of the active phase on the supports and the pore size distribution of the supports.[45,46] It should be noted that there are many investigations in the gas-phase dehydration of glycerol to acrolein which were conducted mostly at high temperature and ambient pressure conditions as reviewed by Katryniok *et al.*[57]

Hydrothermal conversion with base catalysts

Lactic acid is receiving more and more attention as the raw material monomer for producing biodegradable poly (lactic acid). It was reported that carbohydrates were converted to lactic acid with base catalysts.[58,59] In the presence of a base catalyst, lactic acid can also be produced from glycerol under hydrothermal conditions. Table 2 gives typical results of base-catalytic hydrothermal conversion of glycerol. High lactic acid yield (up to 90%) can be obtained from glycerol by basic hydrothermal process.

Basic hydrothermal process

Acid catalysts were widely used in hydrothermal conversion of glycerol. However, much fewer studies were reported on base-catalytic hydrothermal conversion of glycerol.[60] Since homogeneous basic catalysts are used in commercial biodiesel production, after reaction, they are

Table 2. Typical results of base-catalytic hydrothermal conversion of glycerol.

Catalyst	T (K)	P (MPa)	Reactor type	Time (min)	C (%)	Y (%)	Ref.
NaOH	573	9	Batch	90	100	90	[60]
KOH	573	9	Batch	90	100	90	[61]
$Ba(OH)_2$	573	9	Batch	90	100	38	[61]
NaOH	553	7	Batch	90	100	84.5	[62]
Na_2SiO_3	573	9	Batch	90	100	90	[67]
NaOH (Cu_2O)	473	1.4	Batch	360	95.1	76.4	[94]
NaOH	553	10	Batch	90	84	34.7	[69]
NaOH	553	10	Flow	90	92	16	[72]

T: reaction temperature; P: reaction pressure; C(%): glycerol conversion rate = (moles of glycerol converted/total moles of initial glycerol) × 100; Y(%) lactic acid yield = (moles of lactic acid formed/total moles of initial glycerol) × 100.

hard to be recovered for reuse. Effective use of these basic effluents for converting the biodiesel by-product glycerol to chemicals such as lactic acid will reduce pollution and cost of the whole process.

Mechanism of lactic acid formation

Kishida *et al.*[60] converted glycerol to lactic acid in subcritical water with a base catalyst (NaOH), and proposed a reaction mechanism (Fig. 5). Glycerol is first decomposed to pyruvaldehyde with elimination of hydrogen by an [H^-] shift to the adjacent hydrogen. Pyruvaldehyde formed is then converted into lactic acid ion by the benzilic rearrangement. The dehydrogenation of glycerol to glyceraldehyde is a key step in the hydrothermal reactions. In the presence of a base catalyst, both dehydrogenation of glycerol to glyceraldehyde and conversion of glyceraldehyde to lactic acid are promoted by hydrothermal medium.[61,62] In addition to the gaseous product of hydrogen with similar molar yield as that of lactic acid, small amounts of pyruvaldehyde, formic acid, acetic acid and acrylic acid are observed. These organic acids probably are produced from the decomposition of lactic acid. First, in high-temperature water, lactic acid is converted to acetaldehyde and acrylic acid through decarboxylation and dehydration, respectively. Then, formic acid and acetic acid are formed by oxidative cleavage of acetaldehyde and acrylic acid.[63–65]

Influence factors on lactic acid production

Optimization of operating conditions

First, the basic hydrothermal decomposition hardly occurs below 533 K, indicating that high-temperature water plays a large role in these reactions.[60,66] As temperature increases (e.g. 553 or 573 K), the yield of lactic acid increases substantially. Secondly, catalyst concentration is an important factor in the basic hydrothermal reactions. A high lactic acid yield of 90 mol% at 573 K, was obtained with a NaOH concentration of 1.25 M.[60,61] One reason is that dehydrogenation of glycerol catalyzed by [OH^-] is a crucial step in the reaction route. Another possible reason is that the lactic acid formed can consume NaOH by neutralization. However, no significant increase in the yield of lactic acid is observed when the initial concentration of [OH^-] is higher than 1.25 M.[60] Thirdly, the influence of glycerol concentration on lactic acid yield should be taken into account. According to the results from Kishida *et al.*[60] and Shen *et al.*,[61] initial glycerol concentration at 0.3–3.5 M has no influence on reaction pathways. A relatively high glycerol concentration resulting in high lactic acid yield is necessary for an industrially feasible process.[62] Finally, the yield of lactic acid increases with reaction time until the maximum yield. Then, the yield decreases steadily due to the secondary decomposition.

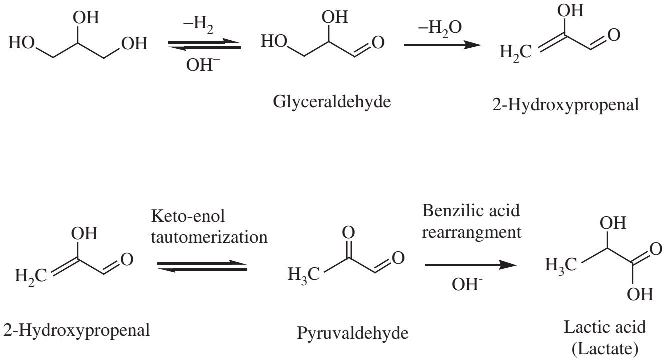

Figure 5. Basic hydrothermal conversion of glycerol to lactic acid.[60]

Effects of base catalyst

Shen *et al.*[61] studied the hydrothermal conversion of glycerol to lactic acid by using alkali-metal hydroxides and alkaline-earth-metal hydroxides. Their results showed that the lactic acid yield is strongly dependent on the [OH^-] concentration. Therefore, alkali-metal hydroxides have much better catalytic performance because of their stronger alkalinity and higher solubility in water than alkaline-earth-metal hydroxides. For instance, no lactic acid yield was observed by using $Al(OH)_3$ due to its amphoteric character and low solubility in water. Furthermore, it was found that KOH was more effective than NaOH for the hydrothermal production of lactic acid.

In our work, we found that sodium silicate (Na_2SiO_3) can catalyze the hydrothermal conversion of glycerol to lactic acid.[67] Lactic acid with 90% yield was achieved at 573 K for 90 min with an initial concentration of sodium silicate of 0.625 M. Compared with alkali-metal hydroxides (e.g. NaOH or KOH), the process of hydration of sodium silicate is different and proceeds in the following three steps:[68]

$$\equiv Si{-}O{-}Na + H_2O \rightarrow \equiv Si{-}O{-}H + [OH^-] \quad (1)$$

$$\equiv Si{-}O{-}Si\equiv + [OH^-] \rightarrow \equiv Si{-}O{-}H + \equiv Si{-}O^- \quad (2)$$

$$\equiv Si{-}O^- + H_2O \rightarrow \equiv Si{-}O{-}H + [OH^-] \quad (3)$$

Such series of reactions produce [OH^-] which plays a critical role in the subsequent hydrothermal conversions. From the equations and experimental results, we found that sodium silicate was more active than NaOH or KOH in the hydrothermal conversion of glycerol to lactic acid because only half of the catalyst was used.

Effects of metal ions

Shen *et al.*[61] studied the effects of metal ions on the solubility of hydroxides or reaction mechanism. The catalytic activity follows the orders: KOH > NaOH > LiOH for alkali-metal hydroxides, and $Ba(OH)_2 > Sr(OH)_2 > Ca(OH)_2 > Mg(OH)_2$ for alkaline-earth-metal hydroxides (e.g. the lactic acid yield is 90% and 38% with KOH and $Ba(OH)_2$, respectively). These orders agree with the hydroxide solubility at low temperatures, and may imply that they have similar solubility orders in hydrothermal water. For $Ca(OH)_2$ and $Mg(OH)_2$, the lower conversion rate of glycerol of $Mg(OH)_2$ than $Ca(OH)_2$ is probably due to their different metal ionic radii and different solubilities. In the case of $Ba(OH)_2$ and $Sr(OH)_2$, hydrothermal conversion of lactic acid was induced to form formic and acetic acids.

Basic hydrothermal electrolysis

Compared with ambient liquid water, subcritical water possesses unique physicochemical properties such as lower dielectric constant, diminishing hydrogen bonds and higher [H^+] and [OH^-] ion concentration, which can minimize the amount of energy consumption for electrolysis. From the perspective of economic feasibility, subcritical water can be selected as a good reaction medium for hydrothermal electrolytic reactions.

Mechanism of lactic acid formation

Yuksel *et al.*[69] developed a new hydrothermal electrolysis process where glycerol can be converted to lactic acid and other value-added chemicals. In their system, reduction and oxidation reactions are as follows:

$$\text{Reduction reaction (Ti beaker): } 2H_2O + 2e^- \rightarrow H_2(g) + 2[OH^-] \quad (4)$$

$$\text{Oxidation reaction (Ir electrode): } H_2O \rightarrow 1/2O_2(g) + 2[H^+](aq) + 2e^- \quad (5)$$

$$\text{Electrolysis of water: } H_2O \rightarrow H_2 + 1/2O_2 \quad (6)$$

In the cathodic compartment, water is reduced to hydrogen in titanium beaker according to Eqn (4), whereas in the anodic compartment (Ir electrode), oxygen is produced through water oxidation (Eqn (5)). Water is electrolyzed to H_2 and O_2 according to the overall reaction (Eqn (6)).[69, 70]

The possible reaction pathway for the production of lactic acid under basic conditions is shown in Fig. 6. Glycerol is transformed to glyceraldehyde and glycolaldehyde in the presence of oxygen generated from the electrolysis of water. After that, the intermediate glyceraldehyde is converted to pyruvaldehyde which is further converted to lactic acid.[60] Besides, lactic acid also may be formed from glycolaldehyde by basic hydrothermal reaction.[71] Other liquid products such as formic acid, glycolic acid and acetic acid are produced too.

Parameter influence on lactic acid production

Effects of electrolysis current and base concentration

The conversion rate of glycerol and yield of lactic acid under basic conditions increase with current value (from 0 to 2 A). However, the yield of lactic acid starts to decrease gradually

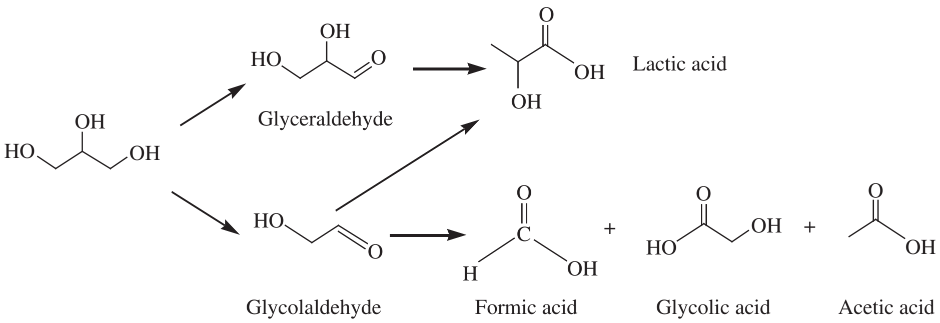

Figure 6. Reaction pathway for the basic hydrothermal electrolysis of glycerol.[72]

with reaction time. It is probably caused by solid residue, such as char formed during reaction that inhibits electrolysis. In addition, high concentration of NaOH enhances the production of lactic acid by hydrothermal electrolysis but with minor effect on the conversion rate of glycerol. In these electrolytic reactions, NaOH concentration should be kept as low as possible (at most 50 mM) because of the corrosion risk in the electrolytic system.[69]

Experimental apparatus

Using an electrolytic autoclave, a maximum glycerol conversion rate of 84% was obtained at 553 K with 50 mM NaOH and 1 A current value after 90 min reaction time.[69] Yuksel *et al.*[72] also used a continuous flow reactor to study the basic hydrothermal electrolysis of glycerol, and more than 92% glycerol was decomposed under the same conditions. Formic acid and glycolaldehyde yields were higher than that of lactic acid in the continuous flow reactor, whereas lactic acid was the main product in the autoclave electrolysis. The advantage of batch reactor is that high current (up to 3 A) could be applied. However, at high current (e.g. current 2 A), product distribution showed wide variation because of char formed that stuck to the electrode and obstructed electrolysis.

Hydrothermal gasification to hydrogen

With the technological advancements in the fuel cell industry, hydrogen from biomass is attracting great interest because of its renewability and carbon neutral nature.[73] Hydrogen can be produced from biodiesel-derived glycerol via hydrothermal gasification processes which include aqueous-phase reforming in subcritical region and SCW gasification.[74] Therefore, in this section, hydrogen production from glycerol in subcritical and supercritical water is introduced.

Aqueous-phase reforming (APR)

Gasification in subcritical water is also called aqueous-phase reforming (APR). Dumesic *et al.*[75] studied hydrogen production from alcohols and sugars from 498 to 538 K and 2.9 to 5.6 MPa using a platinum-based catalyst. In their work, 99% conversion rate of glycerol (1 wt%) with 51% selectivity to H_2 was achieved at 538 K and 5.6 MPa. Later, they used inexpensive Raney Ni-Sn catalyst to gasify biomass-derived hydrocarbons, including glycerol.[76] Complete conversion of glycerol with 76% selectivity to H_2 at 538 K and 5.14 MPa was achieved. In addition to the low reaction temperature, APR process can promote the water-gas shift reaction to decrease the amount of CO. It was found that CH_4 selectivity increased at higher temperatures and pressures. Furthermore, a high H_2 selectivity of 70% at 77% conversion rate of glycerol was obtained when 10 wt% of glycerol was used. However, the amounts of CO and CH_4 increased substantially when the feed concentration of glycerol was up to 30 or 50 wt%.[77]

Wen *et al.*[78] studied the effects of Pt, Ni, Co and Cu catalysts and their supports on APR process of glycerol using a fixed-bed flow reactor. They found that the activity of the four metal catalysts increased in the order of Co, Ni, Cu, and Pt. Moreover, it was found that a higher hydrogen formation rate as well as a higher hydrogen molar concentration was achieved because of absorption of CO_2 by using a basic support, whereas an acidic or neutral support tended to increase the alkane formation. Navarro *et al.*[79] reported that a highest glycerol conversion rate (37%) was achieved over Ni catalyst supported on alumina modified with La in APR processing of 1 wt% glycerol. APR of glycerol to hydrogen on several Pt based catalysts was also studied by Lehnert and Claus.[80] In their work, they found that H_2 selectivity increased with increasing catalyst particle size from 1.6 to 3.1 nm. Also, the mixture of γ-, θ-, and δ- phase of alumina led to an increase in H_2 production as compared with pure γ-alumina. Luo *et al.*[81] examined the effects of metal loadings and operation conditions on APR processing glycerol over series of Al_2O_3-supported Pt catalysts. Their results showed that hydrogen generation is accompanied by other parallel reactions such as dehydration, hydrogenation, and methanation to form alkane and liquid products. It was also found that new phase of boehmit $Al_2(OOH)_2$ and carbonaceous entities were formed on the catalysts resulting in the catalyst deactivation. Menezes *et al.*[82] studied hydrogen production from APR of glycerol over Pt catalysts supported on different oxides (Al_2O_3, ZrO_2, MgO and CeO_2). The Pt catalysts supported on MgO and CeO_2 presented good activity in hydrogen production and selectivity. Their experiments further confirmed that the nature of the support influences the catalytic performance on APR of glycerol. Manfro *et al.*[83]

reported that CeO_2-supported catalysts showed higher hydrogen production and less formation of methane than alumina-supported nickel catalyst. APR of glycerol over Ni-Co bimetallic catalyst was reported by Luo.[84] This bimetallic catalyst not only possessed good ability of C-C breakage due to Nickel metal, but also improved hydrogen selectivity because of cobalt metal. In addition, cerium doping on the cobalt catalyst would increase its catalytic activity and suppress methanation.

High temperature (up to supercritical region) can promote gasification even without adding any catalyst. The supercritical water gasification (SCWG) is introduced next.

Supercritical water gasification (SCWG)

SCW gasification of biomass was reviewed extensively.[38,85,86] Here, we only briefly introduce SCWG of glycerol. Kersten *et al.*[87] reported that dilute glycerol could be completely gasified in SCW without adding any catalyst. Addition of alkali catalysts (e.g. K_2CO_3) that promotes water-gas shift reaction would enhance glycerol gasification efficiency and increase hydrogen yield in SCWG process.[88] However, these alkali salts would inhibit gasification at lower temperatures.[89]

Byrd *et al.*[90] studied hydrogen production from glycerol by SCWG over Ru/Al_2O_3 catalyst. In their work, 6.5-mol hydrogen/mol-glycerol was obtained at 1073 K and 24.1 MPa. They also found that hydrogen yield increased with temperature, and methanation was suppressed by operating at short residence time. Hydrogen production from glycerol in SCWG process over Ru/ZrO_2 catalyst was examined by May *et al.*[91] Complete conversion of glycerol was achieved at temperatures of 783 or 823 K and pressure of 35 MPa with 1 wt% Ru/ZrO_2 catalyst. In addition to H_2 and carbon oxides, water-soluble products like acetic acid and acetaldehyde were formed. Carbon deposition was also observed on the surface of the inert zirconia particles which resulted in decreasing hydrogen yield due to tar formation.

Typical results of catalytic hydrothermal gasification of glycerol are summarized in Table 3. Hydrogen gas (20–100% convertion rate with 26.1–95% selectivity) can be efficiently produced from glycerol by APR process (493–543 K, 2–6 MPa) or SCW gasification (e.g. 823 K and 35 MPa). APR process occurs at low temperature which reduces energy requirements and minimizes the complexities of operation but catalysts are required. At higher temperatures, hydrogen

Table 3. Typical results of catalytic hydrothermal gasification of glycerol.

Catalyst	Glycerol (wt%)	T (K)	P (MPa)	Reactor type	Time	C (%)	S (%)	Ref.
Pt/γ- Al_2O_3	1	538	5.6	Flow	0.008^a	99	51	[75]
Raney Ni-Sn	1	538	5.14	Flow	10.3^b	100	76	[76]
Pt/HUSY	10	503	3.2	Flow	8.4^b	22	–	[78]
Ni/Al_2O_3-La_2O_3	1	498	3	Flow	1.25^a	37	–	[79]
Pt/Al_2O_3	10	523	2	Flow	1–4 h	45	85	[80]
Pt/γ- Al_2O_3	10	493	2.5	Flow	10–14 h	42	95	[81]
Pt/MgO	1	498	2.3	Batch	3 h	20	–	[82]
Ni/CeO_2	1	543	5.2	Batch	4 h	30	–	[83]
Ni-Co	5	493	2.5	Flow	2 h	50	85	[84]
Pt-Re/C(KOH)	10	498	2.9	Flow	5^a	34.3	26.1	[99]
Ru/Al_2O_3	40	1073	24.1	Flow	1 s	–	–	[90]
Ru/ZrO_2	5	823	35	Flow	8 s	–	–	[91]
Na_2CO_3	20	923	27	Flow	6 s	–	–	[109]
K_2CO_3	10	923	25	Flow	8 s	96%	–	[88]

T: reaction temperature; P: reaction pressure; C(%): C conversion to gas = (C in gas phase/total C fed into reactor) × 100; S (%): H_2 selectivity = (molecules H_2 produced/C atoms in gas phase) (1/R) × 100, where R is the H_2/CO_2 reforming ratio of 7/3 for glycerol.

[a] Weight hourly space velocity ($m_{glycerol}\ m_{catalyst}^{-1}h^{-1}$).

[b] Liquid hourly space velocity ($V_{feed}\ V_{catalyst}^{-1}h^{-1}$).

can be generated by SCWG with more concentrated glycerol and shorter reaction time even without catalyst.

Future perspectives and suggestions

As summarized in Fig. 7, hydrothermal conversion of glycerol in subcritical and supercritical water is a promising process for obtaining value-added chemicals and hydrogen. However, there are several important issues should be considered and resolved before its commercial applications.

Applications of heterogeneous catalysts

It is well-known that glycerol is stable in high-temperature and high-pressure conditions, so, it is recommended to add acid or base catalysts in hydrothermal reactions to promote its conversion.

(a) In the dehydration of glycerol with acids, owing to technical and environmental limitations, such as reactor corrosion, catalyst reusability and waste management, homogeneous acids or salts are not the desirable catalysts for practical applications. Heterogeneous acidic catalysts can be used with distinct advantages in recycling, separation, and environmental friendliness. They are easily separated from the products mixture for recycling after reaction. As an example, heteropolyacids (HPAs) have great potential as heterogeneous catalysts in the dehydration of glycerol due to their high Brønsted acidity and well-known structures.[92] However, leaching of the acid sites and the formation of coke under hydrothermal conditions will deactivate the catalysts. High-efficient and stable heterogeneous acid catalysts should be developed to solve the problems. A good heterogeneous catalyst with sufficient catalytic activity combined with appropriate reactor design should make it possible to realize the dehydration of glycerol on a practical scale.

(b) In the case of base-catalyzed hydrothermal reactions, heterogeneous basic catalysts have similar advantages for applications.[93] However, there is no report for their uses on the production of lactic acid from glycerol. Recently, Roy *et al.*[94] reported a catalytic route for glycerol conversion to lactic acid with Cu-based catalysts in basic hydrothermal medium. A high yield (80%) of lactic acid was obtained at 473 K, much lower than that

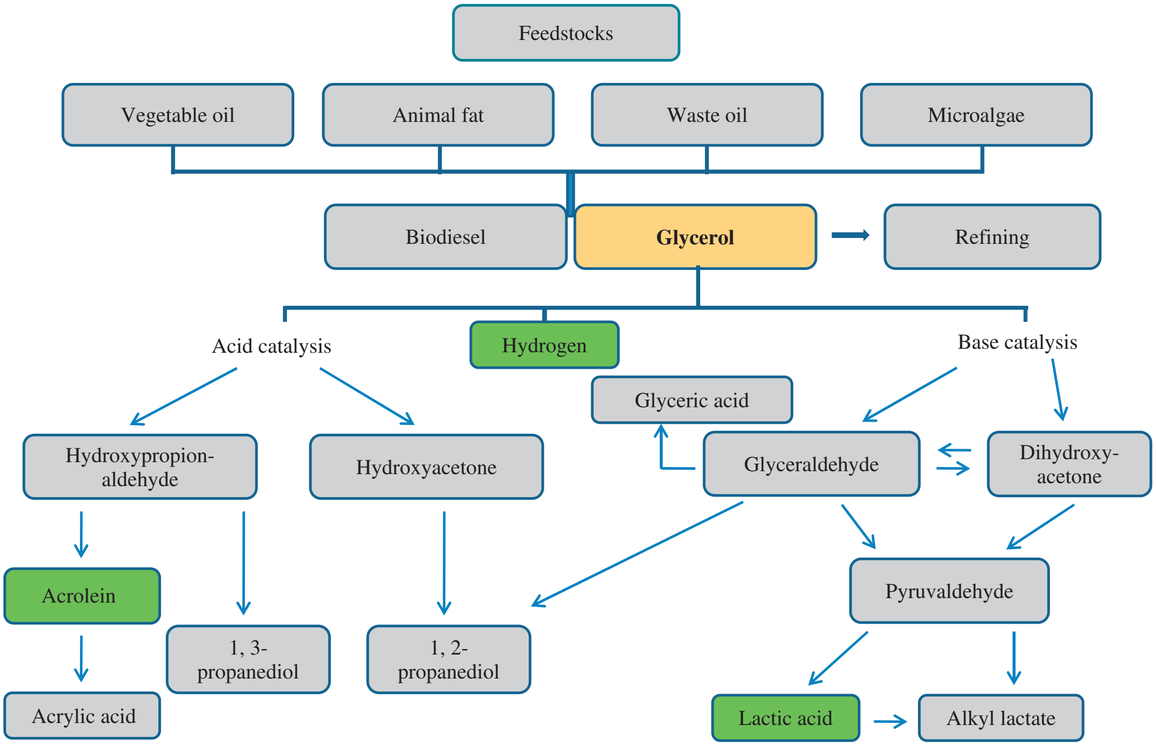

Figure 7. A schematic diagram of a biorefinery for biodiesel-derived glycerol under hydrothermal conditions.

(573 K) given by Shen *et al.*[61] Besides, the Cu-based catalysts with excellent recyclability and stability resulted in identical glycerol conversion rate and lactic acid selectivity during the recycle runs. These results indicated that Cu-based catalysts can promote the initial dehydrogenation of glycerol at lower reaction temperatures in the presence of a base (e.g. NaOH). So, utilizing a metallic catalyst with a basic aqueous solution or directly using a heterogeneous basic catalyst (e.g. activated hydrotalcites) might provide a new idea for the basic hydrothermal processing of glycerol.

Some approaches for product separation

The separation and purification of products after hydrothermal reaction is a critical issue, as it directly influences the production cost and feasibility of the hydrothermal process. Some methods can be used to improve the problem.

(a) A new approach to separate products in acid-catalyzed dehydration is the production of acrylic acid that is easier to be separated than acrolein and it is also used as an important chemical intermediate.[95,96] The overall transformation formally includes the first-step of dehydration into acrolein, and the second oxidation step into acrylic acid (Fig. 7). In this process, a single bifunctional-catalyst is used to meet the need for the new catalytic approach that combines several chemical steps into a single catalyzed transformation. However, a low yield (25–28%) of acrylic acid was achieved with severe deactivation of the catalyst. In addition, a large amount of other oxidation products would be produced in the second step. So, further efforts in developing a stable catalyst and increasing the selectivity to acrylic acid should be made before this process become economically feasible.

(b) The economic production of lactic acid depends on its effective separation and purification. Many traditional separation techniques such as electrodialysis, membrane separation, ion exchange, reverse osmosis, and evaporation were complicated and expensive. An alternative process is to form lactic ester (e.g. methyl lactate) that is purified further by distillation. One-pot formation of methyl lactate from triose sugars (e.g. glyceraldehyde), was studied recently.[97,98] The reaction formally comprises dehydration and esterification to methyl lactate. This novel technology has considerable prospects because of its low energy consumption, low investment and easy separation (Fig. 7).

(c) Without further separation, the effluent (i.e. crude glycerol, methanol and others) can be directly gasified. In hydrothermal gasification process, gas is automatically separated from product mixture, but increasing hydrogen yield and purity is still an important issue. An addition of base such as KOH will enhance hydrogen productivity due to the CO_2 sorption to promote water-gas shift reaction.[99] Therefore, in order to produce CO_2-free biofuel hydrogen, the method of CO_2 removal is recommended to be applied in glycerol hydrothermal gasification. In practical processes, a heterogeneous basic sorbent such as CaO may be a good option for its low cost and good reusability.

Combination with other reactions

It is a new trend to combine hydrothermal dehydrogenation or dehydration with other reactions such as oxidation, reduction or hydrogenation, which can facilitate to produce other valuable chemicals under controlled conditions.

Combination with oxidation or reduction

In general, hydrothermal reactions under basic conditions using supported metal catalysts combined with oxidizing agents such as air, oxygen and hydrogen peroxide are favorable for the oxidation of glycerol.[100] The process consists of the dehydrogenation of glycerol and subsequent oxidation of the formed intermediate. Therefore, the basic catalyst plays an essential role for the start of the reaction during the overall catalytic glycerol oxidation. Shen *et al.*[101] developed a new efficient approach to the synthesis of lactic acid from glycerol oxidation under basic conditions. The first-step proceeds, by an oxidative dehydrogenation of glycerol to glyceraldehyde and dihydroxyacetone intermediates, then by base-catalyzed reactions of these intermediates to lactic acid, instead of oxidation to yield glyceric acid (Fig. 7). So, it provides a potential industrial practice to produce lactic acid at much lower temperatures.

A new strategy for reduction of CO_2 contributed to global warming to value-added product formic acid, whereas conversion of glycerol to lactic acid under hydrothermal basic conditions (573 K) has been proposed by Jin and her co-workers.[102] In their process, carbon dioxide is ultimately reduced to formic acid in the presence of NaOH, and glycerol using as a reducing agent, is efficiently converted to lactic acid. It indicates that both CO_2 (greenhouse gas) and glycerol (by-product of biodiesel) can be effectively utilized simultaneously by basic hydrothermal processing.

Combination with hydrogenation

Propylene glycols (herein refer to 1, 2-propanediol and 1, 3-propanediol), used as important chemical commodities, can be selectively transformed from glycerol by hydrogenation routes.[103] Miyazawa *et al.*[104] studied the combination of hydrothermal dehydration with hydrogenation conversion of glycerol under acidic conditions in the presence of hydrogen (393 K and 8 MPa). Value-added products such as 1, 2-propanediol, 1, 3-propanediol, and other degradation products are obtained during the reactions. First, the dehydration of glycerol to hydroxyacetone or hydroxypropionaldehyde is catalyzed by an acid catalyst. Then, the subsequent hydrogenation of hydroxyacetone gives 1, 2-propanediol, while 1, 3-propanediol is formed by the hydrogenation of hydroxypropionaldehyde (Fig. 7).

Concerning the basic conditions, the whole reaction process involves the dehydrogenation of glycerol to glyceraldehyde and subsequent hydrogenation to form 1, 2-propanediol in the presence of hydrogen (Fig. 7). In addition to lactic acid (lactate) formed as a main product, ethylene glycol was also hydrogenated by the cleavage of C-C bonds from glycerol.[105]

Therefore, it is another alternative route to increase the profitability of glycerol utilization under hydrothermal conditions.

Reactors

From an industrial point of view, types of reactors, reactor corrosion and operation in industrial production should be fully considered.

Batch process vs flow process

The batch process with simple construction and easy operation usually provides high conversion rate of glycerol at low temperature for long reaction time (e.g. 10 h) even without catalyst. Besides, high concentration of glycerol can be used in a batch process. For hydrothermal electrolysis, a batch process is preferred to produce lactic acid.[71] However, slow heating rate and interrupted operation limit its applications.

Flow reactors can produce products continuously with high efficiency in seconds (Tables 1–3). It is easy to control reactions in a flow process, such as heating rate, temperature and pressure as well as quick removal of products to avoid secondary decomposition. Glycerol is easily and rapidly heated to high temperature and converted to targeted products immediately. For hydrothermal gasification, a flow process is first considered.[106] However, conversion rate as well as hydrogen selectivity is decreased and coke is formed to plug reactor when high concentration of glycerol is used.

Reactor corrosion

Hydrothermal water with higher $[H^+]$ and $[OH^-]$ ion concentration will cause metal corrosion. The presence of an acid or base compound intensifies the corrosive issue, with a salt catalyst having the same corrosion problem even though it is relative low.[107] So, a stable high-performance heterogeneous catalyst is more desirable in practical applications. Although the materials of the stainless-steel reactor containing Fe and Ni had no significant effect on the basic hydrothermal conversion of glycerol,[61] the reactor must be specifically designed.

Crude glycerol as raw material

Glycerol obtained from the biodiesel industry is impure, containing inorganics like water and salts, and organics like esters, fatty acids, and methanol. Impurities in crude glycerol can greatly influence the conversion of glycerol into other products.[108] Therefore, the handling of the impurities becomes crucial. Crude glycerol has proved to be a viable alternative for producing hydrogen; however, inorganic salts (e.g. NaCl) can cause catalyst poisoning and reactor plugging in hydrogen production from hydrothermal gasification of crude glycerol.[80,109] But, the inorganics can be recovered as fertilizer from the process if managed properly. Another route is removing CO_2 properly to increase hydrogen purity when using crude glycerol after simple batch distillation or evaporation techniques.

Ramírez-López *et al.*[62] used crude glycerol for synthesizing lactic acid under basic hydrothermal conditions. Their results indicated that crude glycerol can be substituted for pure glycerol as raw material. Recently, we found a new process of production of biodiesel and lactic acid from rapeseed oil using sodium silicate as catalyst.[67] Sodium silicate can be easily separated from reaction mixtures in biodiesel production and directly used in the subsequent glycerol conversion. A high lactic acid yield was obtained by using crude glycerol as raw material that contained other components including methanol, soaps and lipids. This research provides another promising option for utilizing crude glycerol directly.

Concluding remarks

The utilization of glycerol for the synthesis of value-added products is a topic of great industrial interest because it can effectively promote the biodiesel industry. Using hydrothermal technology in subcritical and supercritical water, by controlling the reaction conditions (such as pressure, temperature, time, and heating rate), combining with other reactions (e.g. oxidation and hydrogenation), and with base or acid catalysts, can effectively and selectively produce chemicals and hydrogen from glycerol. A heterogeneous catalyzed continuous process combined with efficient product separation shows great potential in the hydrothermal conversion of glycerol. A combination of biodiesel production with subsequent glycerol conversion by directly using the catalyst from biodiesel production is a good option to reduce cost and pollution.

We note that one of the real challenges is that glycerol obtained from the biodiesel industry is always impure. Therefore, a novel process for biodiesel production that can improve the purity of by-product crude glycerol should be studied further. Hydrothermal gasification is an option to gasify impure glycerol. In addition, new application and catalytic conversion based on directly using the catalyst and crude glycerol from biodiesel production need to be developed. Other issues such as corrosion, operation reliability at relative severe conditions and engineering problems should be solved in order to achieve a sustainable and profitable process for the hydrothermal production of value-added chemicals and biofuels.

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