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A Review on Alkyl Levulinates Synthesis from Renewable Levulinic Acid using Various Modified Carbon-Based Catalysts

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Alkyl levulinates have significantly attracted the attention of researchers around the world due to their high potential in various applications especially as fuel-blending chemical to improve fuel properties and performance. Alkyl levulinates can be derived from biomass derivative components such as levulinic acid via alcoholysis reaction. Current research progress on the levulinic acid alcoholysis involves the development of effective catalytic synthesis to improve the levulinates yield. This includes the role of catalyst properties and reaction condition applied during the reaction synthesis. In the last few years, a number of catalysts derived from various types of precursors have been studied to synthesize levulinates from levulinic acid. Catalysts from carbonaceous materials offer several advantages such as environmentally friendly, wide availability, high sustainability, and economical, despite the low alkyl levulinates yield obtained upon the utilization of the catalysts for alcoholysis reaction. Thus, the potential of solid acid carbon-based catalyst has been focused in this review due to the increasing number of applications of carbon-based material as catalyst or catalyst support via various modifications. Extensive research on alkyl levulinates synthesis and applications is required to be emphasized. Therefore, the present article describes the wide potential of alkyl levulinates, fundamental research work, progress research, advantages of alkyl levulinates as a fuel blender, and the future direction for reaction synthesis particularly on the improvement of carbon-based catalyst properties and potential emerging technology.

Key words: Alkyl levulinate; levulinate esters; levulinic acid; esterification; biomass

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In most recent decades, environmental issues such as air pollution, carbon footprint, global warming, climate change, as well as the depletion of non-renewable resources (fossil fuels e.g., coal, petroleum, and natural gas) as a result of excessive consumption, are increasing at an alarming rate. Moreover, the growing intensity of population, urbanization, and industrialization following the flourishing evolution of science and technology has maximized the demand for energy. This scenario has inevitably become one of the main factors upon the exploitation and depletion of natural resources [1-4]. Therefore, instantaneous actions of "green energy strategy" require emphasis in the development and utilization of renewable energy sources in order to minimize the dependence on conventional fuels. Biomass, specifically ligno-cellulosic biomass (LB), is one of the regenerative carbon-based resources currently explored as the most promising feedstock for the production of biofuel and high-value chemicals owing to its advantages of abundant supply and availability, inexpensive, biodegradable, low toxicity, and environmentally friendly [5-7].

The product from the acid hydrolysis of LB (carbohydrates) is C6 sugars, which serve as the feedstock to produce levulinic acid (LA), a top-notch chemical famed as one of the most important platform chemicals [8, 9]. LA is commonly utilized in the production of different types of chemicals, for instance 2-methyl tetrahydrofuran, 2-butanone, succinic acid, valeric acid, and alkyl levulinates (ALs), specifically methyl, ethyl, and n-butyl levulinates which can be synthesized via the esterification of LA with alcohol under acidic catalytic condition [10,11]. Amidst all possible bio-based chemical pathways for ALs synthesis (Figure 1), the alcoholysis of LA has emerged as the most preferred approach among academicians around the world, considering the substantial potential of ALs to be utilized in numerous applications, particularly as fuel and fuel additive, important substance in agriculture and pharmaceuticals, food additives, solvent, polymers, and chemical industries [12,13]. In addition, ALs are also well-known as the "Sustainable Fuel Additives" following its effective implementation as fuel blending chemical by virtue of

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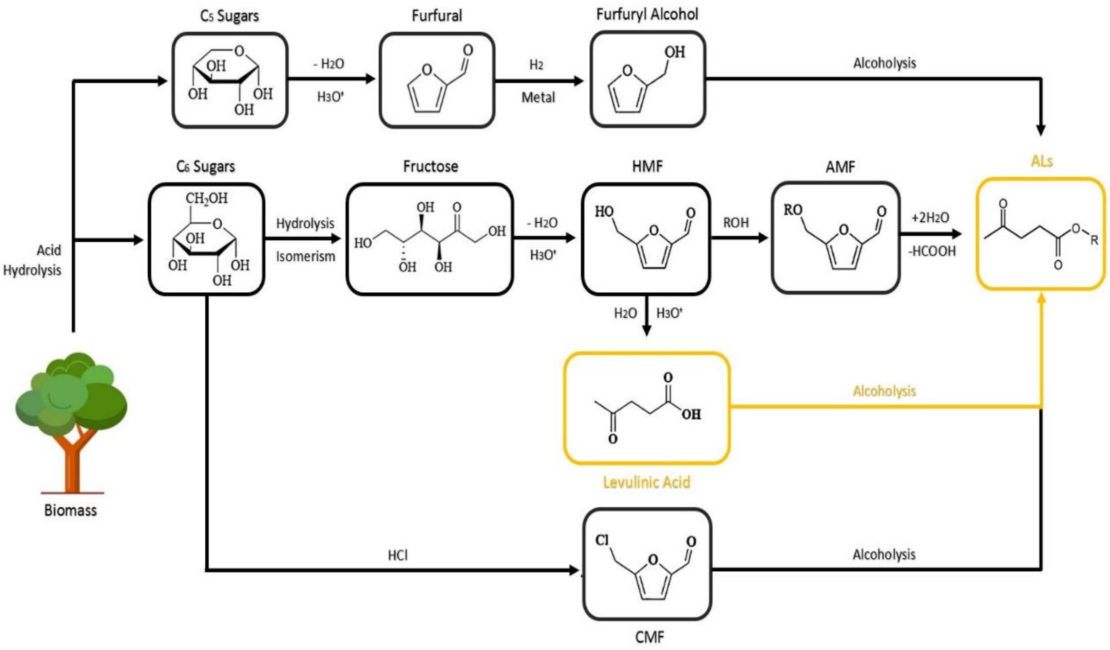

Figure 1. Various bio-based chemical pathways for ALs synthesis (Re-draw from [18])

low toxicity and capability to enhance few major properties such as lubricity, flash point stability, and low temperature flow improver [14,15]. The justification of LA as starting feedstock is attributable to the moderate reaction of the carboxylate group, benefits in terms of end products selectivity [16]. Indeed, as the boiling point of esters is lower than the corresponding carboxylic acid, the separation and purification process via distillation is more practical and cost-effective [17].

On top of that, it is important to analyze the process chemistry of LA esterification in terms of catalyst selection and kinetic study, in particular, to make the manufacturing of ALs commercially attainable. Overall, the most crucial effort is to discover an effective and environmentally friendly catalyst for this process. The catalyst properties of high surface area, porosity, and acid-active sites play an immense role in the overall catalytic activity of LA esterification [19]. The adsorption of LA to the Brønsted acid sites on the catalyst surface would result in the protonation of LA prior to the esterification reaction with the corresponding alcohol to form ALs [20]. Despite that, esterification is also feasible in an uncatalyzed condition, but at longer reaction time. It was reported that the highest conversion of LA (ethyl levulinate) in an uncatalyzed reaction was 60%, achieved at 1 hour reaction time with LA to ethanol ratio of 1:1 and 250 °C temperature. Meanwhile, the reaction equilibrium was observed at only 21%, attained at 60 °C temperature and 120 hours reaction time [21].

In general, two types of acid catalysts namely homogeneous catalysts (mineral acids, organic acids, metal triflates, metal chloride, and ionic liquids) and heterogeneous catalysts (acidic zeolites, acidic resins, acidulated metal oxides, metal oxides, heteropolyacid salts, metal phosphates, functionalized clays, functionalized silica, carbonaceous acids, co-ordination polymers, and magnetic materials) are available to increase the rate of a chemical reaction [5,22,23]. Indeed, heterogeneous catalysts are more preferable in most chemical reactions, considering their easy separation from liquid reaction mixture, higher recyclability, and capability to reduce corrosion in equipment [24]. On the other hand, homogeneous catalysts have been proven superior to heterogenous catalysts in providing better yields in esterification process. This is attributed to the strong Brønsted acidity of these catalysts which contribute to high catalytic activity and selectivity of LA esterification [25]. Nevertheless, the use of mineral acids such as H_2SO_4, H_3PO_4, and HCl permits a number of critical drawbacks such as promoting corrosion in equipment, complicated separation and disposal processes, and lower recyclability which incurs higher cost ALs synthesis [26-30]. Thus, the development and substitution of recyclable, environmentally friendly, and non-corrosive homogeneous catalysts over heterogeneous type is preferable to establish a green esterification process of LA.

Among the available heterogeneous catalysts, carbon-based catalysts derived from carbon materials are prominent in research works owing to their low-cost, high sustainability, abundant source of feedstock, excellent chemical stability (inert in strong acid and basic conditions), and versatile surface modification (functional group, acid, enzymes, metallic metals, polarity or hydrophobicity) aiming to improve the catalytic activity [24,31-33]. Besides, as shown in Figure 2, the applications of carbon materials are vast.

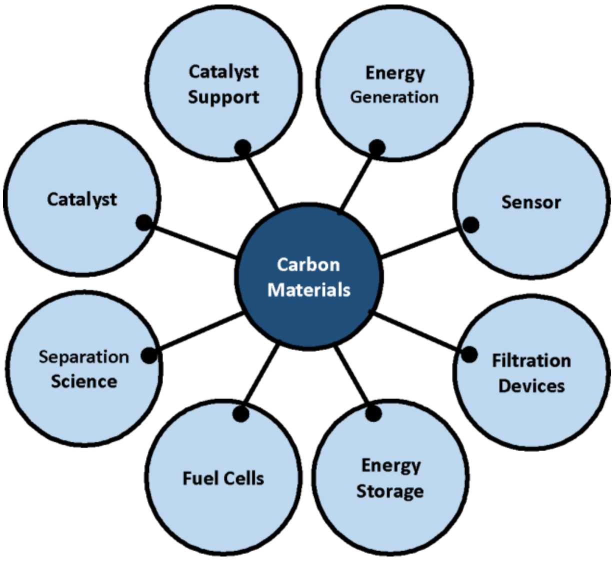

Figure 2. The vast applications of carbon materials [31]

Carbon-based catalysts are also competent in many chemical and biochemical processes due to their high surface area and porosity, assigning them as one of the effective heterogeneous catalysts [34]. Carbon-based catalysts can be produced from the sulfonation of any types of carbon-based matter including biomass wastes (e.g., forest, plant, agricultural, and marine wastes) and industrial wastes (e.g., ash and coal) by incorporating H_2SO_4 in the pore structure of carbonaceous materials for strong attachment of –SO_3H groups [35,36]. Currently, agricultural wastes have drawn a lot of attention as a carbon precursor, where a number of potential biomass wastes such as palm kernel shell, coconut coir husk, bamboo, cacao shell, etc. were highlighted in prior studies [37]. On top of that, sulfonated carbon-based catalysts exhibited superior performance of LA esterification by yielding shorter alcohol (methanol and ethanol) chains compared to other solid acid catalysts. This was observed from the perspective of strong acid site by using ammonia-temperature programmed desorption (NH_3-TPD), for example Amberlyst-15 (macroreticular polystyrene with strong sulfonic group), mesoporous silica (SBA-15), SAC-13 (SiO_2 supported Nafion), and zeolite Beta [23]. Moreover, sulfonated carbon-based acid catalyst is documented as an effective catalyst for the ethanolysis of LA to ALs on the basis of its thermal stability, water tolerance, high acid site, and excellent catalytic performance [35,38, 39]. The high acidity property of the catalyst is ideal to enhance the yield of ALs, even so the treatment condition and initial material also contribute to the efficiency of the catalyst [40-42]. Therefore, the fundamental of this review paper is to describe the potential and useful data for the forthcoming strategies of ALs synthesis including the ALs reaction synthesis, potential applications of ALs, as well as the improvement of carbon-based catalyst properties in favor of implementing potential emerging technology for the reaction.

1.0. Alkyl Levulinates (ALs) and Their Potential Applications

ALs are well-known as ‘sustainable fuel additives’ which contribute tremendous positive impact on the commercialization of levulinates. Based on the market analysis report by Grand View Research, the global demand of ALs in 2014 was 32.4 tons/year (equivalent to USD 8.8 mil) and is projected to grow to 49.1 tons/year (equivalent to USD 11.8 mil) by 2022 at the annual growth rate of 5.3%. Furthermore, an analysis report provided by Global Market Insights (GMI) supported the steady growth of ethyl levulinate market as well as the production and applications of ALs [43]. Despite that, the high price of raw materials including LA and the process reaction are hindering the profitability and productivity of ALs, which require attention for future evolution processes. Thus, sustainable and economical synthesis routes of ALs are the main key to magnify the production of ALs industrially.

The initial essences of ALs synthesis are mostly raw biomass (lignocellulose) or biomass derivatives in the presence of catalyst (chemical or biological enzymes). ALs synthesis is achievable by four possible routes: (1) one pot synthesis, (2) alcoholysis of furfuryl alcohol (FAL), (3) reduction of furfural to FAL (4), and esterification of LA, as illustrated in Figure 3 [44]. The first route involves the conversion of cellulose to ALs, which is also known as ‘one pot method’, where raw biomass is added to the reactor all at once while concurrently controlling the reaction conditions [10]. One pot method offers some benefits viz. simple operation (many skippable reaction processes) and low-cost production, and also a few drawbacks like lower yield, lower conversion, low selectivity, and humin formation [45,46]. The second route entails alcoholysis in catalytic system which directly converts furfural alcohol (FAL) to ALs.

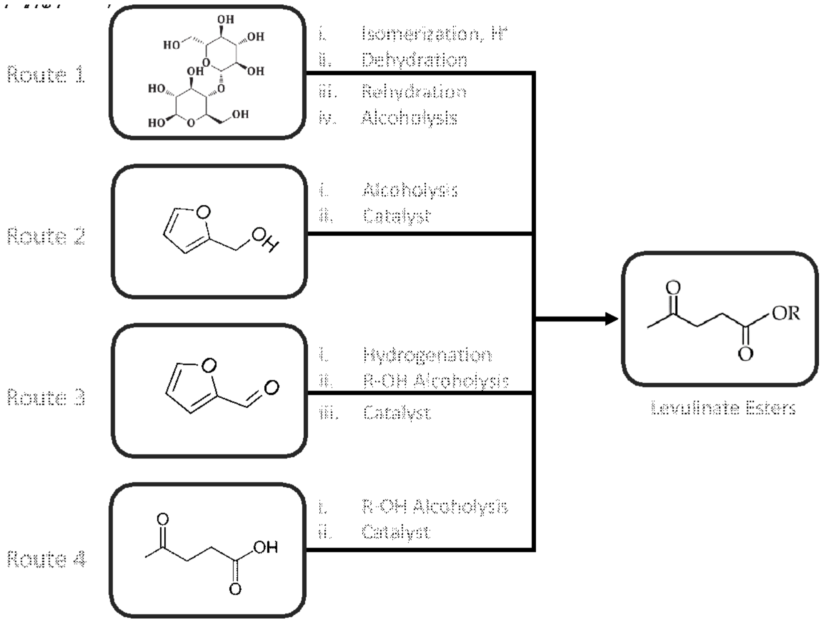

Figure 3. Four possible routes of ALs synthesis [43]

The advantages of this method are its simple reaction, high yield, moderate reaction condition, and low formation of by-products, meanwhile its disadvantage is the availability of FAL as compared to LA feedstock [47]. The third route involves reactions with C5 sugar from acid hydrolysis of biomass prior to dehydration to produce furfural. Furfural is reduced via hydrogenation (liquid or gas phase) to produce FAL, then undergoes alcoholysis to yield ALs. The hydrogenation of furfural via gas phase method is more commonly applied than liquid phase method. This is because high energy consumption is needed for liquid phase hydrogenation method [48]. Meanwhile, the forth route is the most prevalent among all methods because of its simplest and sustainable (availability of LA) approach to synthesize ALs [16]. The esterification of LA, which utilizes various types of acid catalysts, could produce high ALs yield plus water as the by-product [19]. In this review, this route has become the main focus method along with the discussion of carbonaceous material as carbon-based catalysts to synthesize ALs.

ALs including methyl levulinate (ML), ethyl levulinate (EL), and butyl levulinate (BL) are recognized as platform compounds comprising carbonyl and ester groups due to the fact of their potential applications in numerous industries as shown in Figure 4. These include bio-lubricants, chemical reagent, polymer precursor, mineral oil refining, foam comprising material, green solvents, resin precursors, plasticizer, fragrances, pharmaceutical, cosmetics, food flavoring agent, herbicides synthesis, and fuel-blending component, which is the main focus in this paper [43,49,50]. Indeed, conventional diesel engine generates excessive NO_X and carbon monoxide (CO) which brings upon negative impacts to the environment. Alternatively, the incorporation of up to 5 wt.% short carbon chain of ALs (ML or EL) with diesel may improve engine efficiency with relatively lower nitrogen dioxide (NO_2) and carbon monoxide (CO) emissions [49]. ALs also act as fuel oxygenate which enhances fuel combustion, while at the same time reduces exhaust emissions [51]. Moreover, the fusion of ALs with fuel could result in the alterations of fuel qualities, e.g., providing a clean burning of fuel with high lubricity, enhancement in viscosity, excellent cold-flow properties (lower cloud point), decrement of sulfur quantity, and lower heat conductivity [27,52,53].

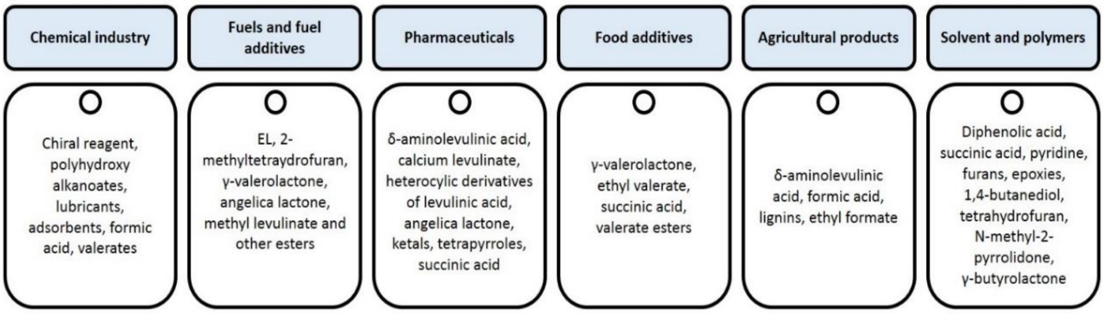

Figure 4. ALs and their potential chemical derivatives for various applications [50]

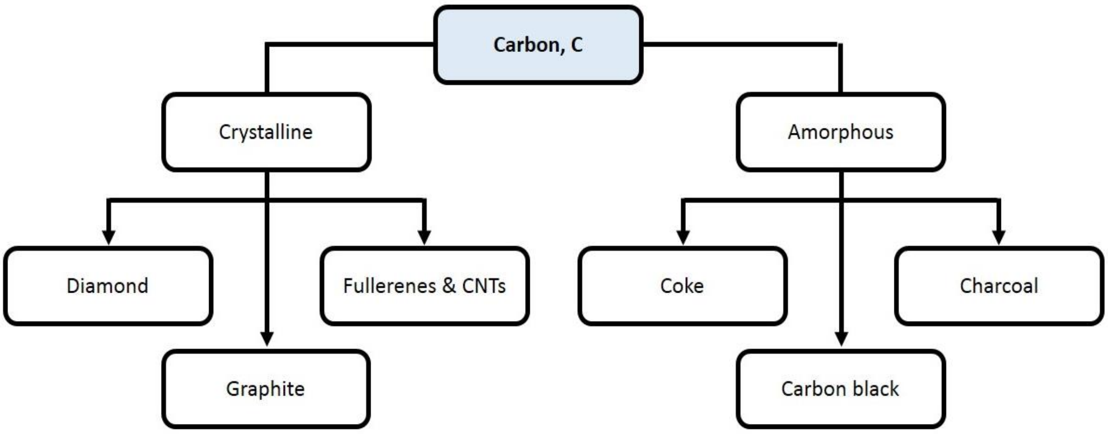

Figure 5. The allotropes of carbon [59]

2.0. Carbon-Based Catalysts and Their Modification for Alkyl Levulinates Synthesis

Carbon, with the symbol of C, is the fourth abundant element on earth. The three most common types of carbon material are diamond, charcoal, and graphite. In the perspective of chemistry, carbon is categorized based on the arrangement of atoms and hybridization state as demonstrated in Figure 5 [54, 55]. The classes of carbon porous material are sorted based on the pore structure, namely miroporous (diameter < 2 nm), mesoporous (diameter 2-50 nm), and macroporous (diameter > 50 nm). Among these allotropes, micro-porous and macroporous carbons are found consistently distributed on the surface of activated carbon (AC), a specific form of carbon compound (amorphous) that is extremely compatible in various applications in biomedical appliances, organic dyes, energy sector (fuel cell, energy storage, electro-chemistry), pollution control (waste water treatment, air and gas filter system, toxic compound removal), and specifically as catalyst [56-58]. AC is derived from high carbon content materials including biomass agricultural residues (straw, rice husk, bagasse, miscanthus, bamboo, cotton residue, nut shell, fruit peel, coconut shell, etc.), as well as thermally decomposed coal and petroleum residues. During the heating process of a carbon material, carbonization (formation of porous carbon) occurs, where the water content in the carbon material vaporizes [56].

AC has high surface area, diverse size distribution of pores (good active metal attachment), and various oxygenated functional groups [55,60]. Hence, AC is a perfectly suitable carbon precursor for the production of sulfonated carbon-based catalyst due to its advantages of high heat resistance, large surface area, and inertness in both acidic and basic media [57,61,62]. Moreover, the overall cost for the esterification process could also be reduced by utilizing the catalyst due to its economical price and availability [63]. The proposed structure of AC is illustrated in Figure 6. Furthermore, in a heterogeneous reaction, the application of AC as catalyst might minimize the mass transfer constrain, resulting in higher reaction rate. Recently, the demand for AC as carbon precursor has increased greatly due to its remarkable characteristics and applicability in diverse engineering fields [54].

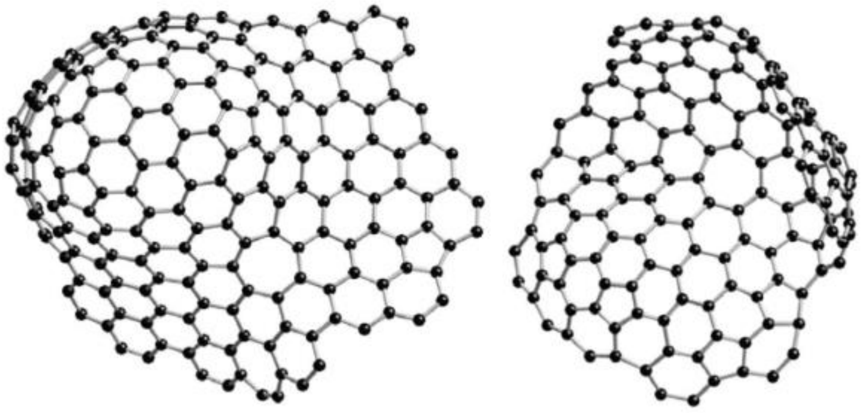

Figure 6. Proposed structure of AC [64]

On top of that, a few techniques are available to produce carbonaceous materials based on the application of the products. For example, (i) direct carbonization (pyrolysis) and hydrothermal carbonization (HTC) produce biochar, hydrochar, liquid bio-oil, and AC, (ii) arch discharge, chemical vapor deposition, and laser ablation produce carbon nanotube (CNT), and (iii) hard template and soft template techniques produce ordered mesoporous carbon (OMC). Among these techniques, pyrolysis and HTC are commonly applied in the production of carbonaceous materials prior to sulfonation, particularly for the application as carbon-based solid acid catalyst [57]. The modification of carbonaceous material is conducted to provide acid site such as Brønsted and/or Lewis acid for the esterification reaction. Sulfonation is commonly used to modify the catalyst and obtain high Brønsted acid which is favourable for high ALs yield. Meanwhile, Lewis acid can be provided such as by metal doping to create active site on carbonaceous material to catalyze the reaction. Catalytic esterification reaction of LA using Brønsted and/or Lewis acid modification influences the reaction performance (reaction activity) which results different ALs yield.

2.1. *Sulfonated Carbon Material as Solid Acid Catalyst*

Sulfonation is a process where carbonaceous material is introduced to a modification agent. The two general methods of sulfonation are direct sulfonation and sulfonation by reduction (alkylation/arylation) [65]. Direct sulfonation on carbon precursors such as AC, lignin, biochar, biomass, and sugar is a more frequent approach as compared to sulfonation by reduction (alkylation/arylation). The process is accomplished by heating carbonaceous material with sulfonating agent (sulfonic group, -SO_3H). Sulfonated carbon-based catalyst was reported to be effective for hydrolysis, nitration, transesterification, and esterification reactions especially for ALs synthesis [56,66]. The proposed structure of sulfonated carbon is illustrated in Figure 7.

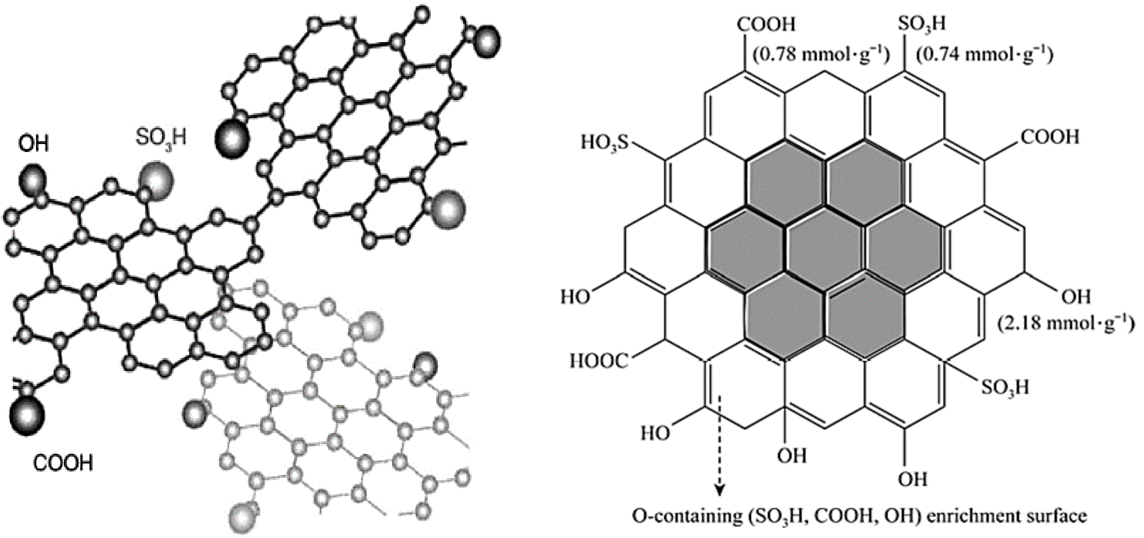

Figure 7. The proposed structure of sulfonated carbon [67, 68]

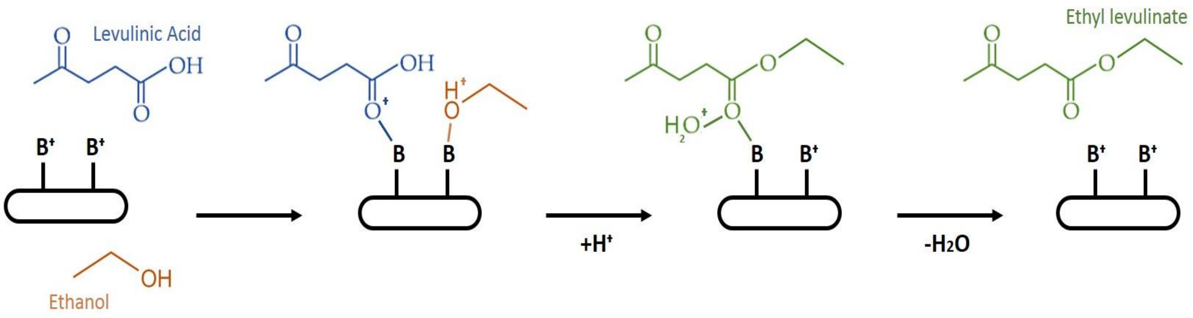

Figure 8. Reaction mechanism of EL over Brønsted acid sites of acidic catalyst

The characteristics of a catalyst is highly influenced by the preparation variables such as carbonization temperature, time, and sulfonation temperature. The number of active sites on catalyst will reduce at high temperature because of the hindered –SO_3H anchoring by the rigid carbon structure. Nevertheless, pyrolysis at lower temperature (400-500 °C) will yield in the formation of cross-linked polymer (soft aggregated) in the catalyst. In addition, the catalyst is highly potential because of its excellent properties such as stable, renewable, safe, low-cost, and simple synthesis routes. Besides, three types of acid sites are present on the surface of sulfonated carbon-based catalyst; strong sulfonic acid (-SO_3H) as the key active site for catalytic reaction, and both phenolic acid (-OH) and weak carboxylic acid (-COOH) as hydrophilic properties improvers to provide higher accessibility of reactants. Figure 8 illustrates a simple diagram to demonstrate the mechanism of EL formation over Brønsted acid sites of acidic catalyst. Generally, the presence of –SO_3H covalent bond improves the catalytic activity and provides outstanding recyclability of the catalyst.

According to Oliveira and da Silva [36], carbon nanotubes (CNTs) have large surface area available for sulfonation. Unfavorably, due to the selectivity and vigorous chemisorption of LA to CNT surface, the overall yield of ALs is low (< 55%) (Table 2 - No. 1). A recent research work by Li et al. [69] proved that sulfonated pine needle (s-PNAC) and loofah sponge (s-p-PNAC) derived carbons exhibited excellent performance of ALs synthesis with 96.1% and 94% of LA conversion, respectively, under optimized condition with good recyclability. The s-PNAC was characterized with amorphous structure and good thermal stability with acid density of 2.28 mmol g^{-1} upon the carbonization of carbon precursor at 700 °C for 90 minutes followed by sulfonation at 160 °C for 15 hours (Table 2 - No. 5 & 6). Meanwhile, Song et al. [70] concluded that an excellent catalytic activity of hollow mesoporous carbon sphere ($ArSO_3H$-HMCSs) was achievable with the combination of well-defined mesoporous structure and strong Brønsted acid. This carbon material consisted of multiple graphene sheets with strong hydrogen bonding between phenolic –OH or –COOH group with –SO_3H group. The reactants (LA and ethanol) and the –OH or –COOH group of the catalyst could create strong hydrogen bonding which encourages reactivity (Table 2 - No. 7). In another work, implementing optimal conditions of 80 °C temperature, 8 hours reaction time, and ethanol to LA molar ratio of 5:1, the LA conversions using corn stalk derived carbons, s-CSC and s-p-CS, were 94% and 93% respectively, with catalyst recyclability of 10 cycles (>90%) (Table 2 – No. 8 & 9) [38].

It was found that the temperature of carbonization of loofah sponge (LSAC) catalyst affected the acid density of the catalyst [62]. The anchoring of –SO_3H group on the catalyst is less effective when the temperature is too low because of incomplete decomposition of cellulose and hemicellulose. However, the carbon content in the carbonaceous material decreases if excessive temperature is applied, thus causes poor sulfonation. The sulfonated LSAC demonstrated excellent catalytic activity with 91% LA conversion (Table 2 - No. 10) when carbonized at 600 °C for 90 minutes followed by sulfonation process. The introduction of –SO_3H group to the catalyst derived sugarcane bagasse (C-SO_3H) showed a vital role to the effectiveness of the catalyst under optimal conditions, where the yield of EL was 88.2 mol% plus 5 times recyclability (Table 2 - No. 11) [71]. The ethanolysis of LA using carbon cryogel produced from urea and furfural (UCC-S) provides excellent performance due to the high acidity from the sulfonation process [40]. As the reaction time increased (2 to 4 hours), the yield of EL has simultaneously increased (17.7 to 99.5 mol%). However, with a further increase in reaction time to 5 hours, the yield has dropped to 76.7 mol% attributed to reversible reaction, where the amount of water molecules developed from the reaction was used up to break the bond of ester to carboxylic acid and alcohol (Table 2 - No. 15). On the other hand, Starbon catalyst (Starbon-400-SO_3H), which was carbonized at 400 °C, possesses special characteristics of adjustable surface properties and large number of microporosity. It was found that Starbon catalyst could yield in 85% conversion of LA (Table 2 - No.17) [72]. BL was successfully synthesized over sulfonated glucose-derived carbon (GC400) catalyst to yield 90.5 % of LA conversion. The sulfonated carbon catalyst contains high density –SO_3H group due to smaller carbon sheets with attachments of weak acid sites (–COOH and phenolic groups) that contribute to the high efficiency of the catalyst (Table 2 - No.18) [73]. In addition, sulfonated catalysts such as sulfonated pyrolyzed cellulose (SCel) and glucose (SGlu), sulfonated HT of glucose (SHTGlu), sulfonated graphene oxide (SGO), sulfonated carbon gel (SCG), and sulfonated activated carbon (SAC) have been derived for the synthesis of ethyl levulinate from LA [23]. Based on their findings, the results were presented as turnover frequency (TOF) values for respective catalysts in the following order: SHTGlu > SCel > SGlu > SGO > SCG > SCNT > SAC. The high density of the functional groups (-SO_3H, -COOH, and –OH) affects the rate of reactions greatly. Based on the overall results described in the abovementioned researches, the sulfonation process of catalyst provided significant results of active catalyst for the esterification reaction of LA to ALs. Various chemicals were explored as the sources of sulfonated group to provide active sites for catalyst precursor especially on carbon materials.

2.2. *Hydrothermal Carbonization (HTC) of Carbon Based-Catalyst*

Hydrothermal carbonization (HTC) is an eco-friendly technology that thermally transforms various types of biomass feedstock into carbonaceous material with no gas emission from solid fuels. HTC is conducted by introducing water to break up the fragmentation of biomass bonds at 180 °C to 250 °C and elevated pressure of 2 to 10 MPa [74]. Indeed, HTC was introduced to convert lignocellulosic biomass into high carbon content material. In a closed vessel, solid with lower oxygen to carbon ratio was formed when the mixture of water and cellulose was heated at 250 °C to 310 °C (Jamari & Howse, 2012). HTC is divided by two processes; (i) direct HTC, where the feed and water are heated in a reactor without catalyst at various temperatures and (ii) catalytic HTC, where catalyst is utilized during the heating process [74]. HTC is applied for various reaction mechanisms such as dehydration, hydrolysis, re-condensation, aromatization, and decarboxylation (A Funke, 2012). The presence of water serves as a reaction medium or reactant to accelerate the carbonization process and produce three types of product; solid (biochar, hydrochar, AC), liquid (bio-oil), and gases [75-77]. The char product formed is dependent on several variables; the process temperature of HTC, biomass to water ratio, type of feedstock, and reaction time [74]. At process temperatures of < 200 °C, hydrochar is produced as the main product, while at process temperature range of 200 to 400 °C (known as hydrothermal liquefaction), liquid hydrocarbon is generated. Meanwhile, HTC carried out at supercritical state of water (known as hydrothermal gasification) produces gaseous products which are not suitable for catalyst synthesis [75]. The hydrochar formed from HTC is preferable to be used as carbon precursor as compared with biochar (product of pyrolysis) because of its low ash content, high hydrophilicity, enhanced dewaterability, and higher energy and mass density [78].

HTC is a suitable method for the synthesis of heterogenous catalyst applied in the esterification of LA. The glucose (HTC-Glu-S), cellulose (HTC-Cell-S), and rye straw (HTC-RS-S) derived catalysts prepared using HTC and sulfonation demonstrated high LA conversion and ester selectivity of >90% (Table 2 – No. 2, 3, 4) [61]. Ogino et al. [23], in their study prepared sulfonated glucose-HTC (SHTGlu) for the esterification reaction of LA to EL, which yielded superior performance based on TOF value compared to other sulfonated catalysts. Meanwhile, hydrothermal carbonization of cellulose as functional carbon material (FCM) was conducted and modified with 5-sulfosalicylic acid dihydrate (sulfonate - S) and ammonium formate (amino - N) either separately or simultaneously [79]. NS-FCM and S-FCM exhibited high total acidity which is near to the acidity of S-ZrO_2 (3.78 mmol g^{-1}), but lower surface area as compared to AC (1300 m^2 g^{-1}). The findings revealed that EL could be yielded in the presence of NS-FCM, S-FCM, and S-AC, but not N-FCM. NS-FCM demonstrated good performance due to the presence of sulfonate group which provides strong acid site with strong specific interaction of LA with amino groups. The results of reaction testing for NS-FCM, S-FCM, N-FCM, FCM, and S-AC are illustrated in Table 2 No. 20 – 24. Based on the findings, the sulfonation of HTC precursor provided an advantage for catalysts to improve its yield up to 59%, while the incorporation of sulfonated amino group has further increased the EL yield to 72%.

2.3. *Functional Carbon Material and Its Modification as Catalyst*

Various types of carbon are synthesized or prepared using different methods, precursors, and conditions to act as catalysts in the reaction conversion of LA to ALs. Carbon precursors usually lack of active sites for reaction, which thus require some modifications. Oliveira and da Silva [36] utilized carbon nanotubes (CNTs) precursor for reaction testing which only yielded 2% of LA conversion. The precursor of HTC carbon from cellulose also provided low reaction yield of 22% at 120 °C temperature and 6 hours of reaction time, which was around the product yield of reaction without catalyst [79]. This scenario shows that modifications are required on the carbon precursor to improve the catalyst properties. The combination of Brønsted and Lewis acid sites is an alternative method to increase the density of active acid sites. The UCC-S-Fe-300 derived from furfural and urea was sulfonated to include Brønsted acid sites, while iron doping was implemented to stimulate Lewis acid active sites for higher efficiency in catalyst (Table 2 – No. 16) [40]. High EL yield of 95.8 mol% was obtained using UCC-S-Fe-300 catalyst, which also provided good reaction yield for the alcoholysis of other biomass derivative components. On the other hand, the acidic ion functionalized N-doped hollow carbon (NHC-$[C_4N][SO_3CF_3]$) exhibited high acid density (2.72 mmol g^{-1}), good stability, large surface area (154 m^2 g^{-1}), and strong Brønsted acid sites [80]. At an optimum condition, the conversion of LA by using the catalyst was achieved at 94.17% and maintained after four cycles (Table 2 – No.19). Calcined carbon cryogel, which was prepared via gel synthesis in acidic condition and calcination at 500 °C for 1 hour, demonstrated excellent properties of large surface area (426.5 m^2 g^{-1}), high acid sites (16.1 mmol g^{-1}), and high thermal stability [81]. Moreover, the calcined carbon cryogel catalyst was highly potential to be applied for the esterification of LA given its high yield of 86.5% (Table 2 – No. 13).

2.4. *Modified Graphene Oxide*

Graphene, which is made up of 2D (two-dimensional) sp2 hybridized carbon atoms, has attracted a great concern to be explored and utilized as a carbon precursor owing to its specialty in terms of its physical, chemical, and electrical characteristics [82].

Graphene oxide (GO), reduced graphene oxide, and exfoliated graphite are the other forms of graphene materials that are currently produced at a high scale. The various applications of GO include energy storage materials, electronic and photonic devices, sensors, and specifically catalyst. Furthermore, GO contains oxygen-containing functionalities (carboxylates, sulfate, alcohols, and epoxides groups) which contribute to its acidic and oxidizing properties [83]. Limited works are available on the esterification reaction of LA in the presence of GO or modified GO catalyst. Previously, Ogino et al. [23] utilized sulfonated graphene oxide (SGO) as catalyst for LA esterification in ethanol, where SGO presented a better performance as compared to other sulfonated catalysts based on the TOF value. According to Zhu et al. [82], GO was utilized as catalyst for furfuryl alcohol alcoholysis with different types of alcohols as shown in Table 1. The catalyst showed an excellent performance (in optimal condition) for the reaction because of its large surface area and highly active acid sites on the surface. This proves the capability of GO or modified GO catalyst for the esterification of LA and alcoholysis of other biomass derivatives.

Table 1. Synthesis of ALs from furfuryl alcohol over GO catalyst [82]

Entry	Alcohol	Product	Yield (%)
1	Methanol	ML	95.4
2	Ethanol	EL	95.5
3	1-propanol	1-propyl levulinate	92.3
4	2-propanol	2-propyl levulinate	91.7
5	1-butanol	1-butyl levulinate	91.4
6	iso-butanol	iso-butyl levulinate	90.0
7	tert-butanol	tert-butyl levulinate	78.2
8	1-pentanol	1-pentyl levulinate	87.9
9	1-hexanol	1-hexyl levulinate	87.0

Table 2. The application of various carbon-based catalysts for LA esterification using different parameters

Catalyst	Carbon precursor	Catalyst loading	Temp. (°C)	Time (h)	Molar ratio[a]	ALs	Conversion yield (%)	Acid density (mmol g^{-1})	Recyclability	Ref.
1) CNT-150	Multiwall carbon nanotube	2.5 wt.%	70	5	5:1	EL	55.0[c]	NA	NA	[36]
2) HTC-Glu-S	Glucose	5 wt.%	60	3	5:1	EL	97.0[c]	NA	NA	[61]
3) HTC-Cell-S	Cellulose	5 wt.%	60	3	5:1	EL	89.0[c]	NA	NA	[61]
4) HTC-RS-S	Rye straw	5 wt.%	60	3	5:1	EL	92.2[c]	NA	NA	[61]
5) s-p-PNAC	Pine needle	5 wt.%	160	24	5:1	EL	96.1[c]	2.08	6 runs, 91.3%	[69]
6) s-PNAC	Pine needle	5 wt.%	80	8	5:1	EL	94.0[c]	2.06	4th run, 63.0%	[69]
7) $ArSO_3H$-HMCSs	Hollow mesoporous carbon sphere	2 wt.%	78	4	7:1	EL	99.9 mol%	NA	10 runs, no major loss of activity	[70]
8) s-CSC	Corn stalk	5 wt.%	80	8	5:1	EL	94.0[c]	2.02	5th run, 36%	[38]

9) s-p-CSC	Corn stalk	5 wt.%	80	8	5:1	EL	93.0[c]	2.00	5th run, 84%	[38]
10) Sulfonated LSAC	Loofah sponge	5 wt.%	80	10	5:1	EL	91.0[c]	1.59	After 4 runs, 56% conversion	[62]
11) C-SO_3H	Sugarcane bagasse	0.3 g	120	9	5:1	EL	88.2 mol%	1.20	Decreased slightly after 5 cycles	[71]
12) Carbon cryogel	Liquified oil palm frond mixture & furfural	35 wt.%	78	5	15:1	EL	71.7 mol%	17.6	After 5 runs, conversion ~65%	[84]
13) Calcined carbon cryogel	Lignin & furfural	15 wt.%	78	10	19:1	EL	86.5 mol%	16.1	NA	[81]
14) Carbon cryogel	Lignin & furfural	15 wt.%	70	10	19:1	EL	80.0 mol%	11.29	NA	[85]
15) UCC-S	Urea & furfural	10 wt.%	80	4	10:1	EL	99.5 mol%	52.1	NA	[40]
16) UCC-S-Fe 300	Urea & furfural	10 wt.%	80	4	10:1	EL	95.8 mol%	75.0	NA	[40]
17) Starbon-400 SO_3H	Mesoporous polysaccharides	0.1 g	80	6	30:1	EL	85[c]	NA	NA	[72]
18) GC400	Glucose-derived amorphous carbon	10 wt.%	100	4	5:1	BL	90.5[c]	1.22	After 5 runs, retained 92%	[73]
19) NHC-$[C_4N][SO_3CF_3]$	N-doped hollow carbon	0.05 g	70	7	15:1	EL	94.17[c]	2.72	After 4 runs, 83.57% conversion	[80]
20) NS-FCM	Cellulose	5 wt.%	120	8	~8:1	EL	72.0	3.44	NA	[79]
21) S-FCM	Cellulose	6 wt.%	120	6	~8:1	EL	59.0	3.54	NA	[79]
22) S-AC	Activated carbon	7.5 wt.%	120	6	~8:1	EL	60.0	2.84	NA	[79]
23) FCM	Cellulose	5 wt.%	120	6	~8:1	EL	22.0	NA	NA	[79]
24) N-FCM	Cellulose	5 wt.%	120	6	~8:1	EL	<8.0	1.9	NA	[79]

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[a] Molar ratio of alcohol to LA, [c] LA conversion

3.0. Kinetic, Thermodynamic, and Mechanism of Alkyl Levulinate Synthesis

The kinetic and thermodynamic parameters and the mechanism of a reaction are parts of its fundamental study which are important to provide a depth understanding on the reactions involved and useful for future reaction process design and upscaling works. Kinetic study has been widely performed on various solid catalysts, but there are still limited works on carbon-based catalyst particularly in LA esterification to ALs. As shown in Table 3, the pseudo-homogeneous kinetic model is commonly employed to represent experimental data. In a prior study, the pseudo-second order kinetic model was applied to represent the reaction of LA to various alkyl levulinate catalyzed by micro/meso HZ-5 [86]. Low activation energy was observed for octyl levulinate (OL) synthesized from LA, followed by BL, EL, and ML. This deduces that the increasing number of carbon chains reduces the activation energy of the reaction. Similar kinetic model was implemented to study the reaction of LA with desilicated HZSM-5 [87] and DPTA/DH-ZSM-5 [88], where low activation energies of 21.1 kJ/mol and 29.4 kJ/mol were obtained, respectively. Kokare et al. [89] revealed activation energies of 34.9 kJ/mol and 39.9 kJ/mol, respectively for the reaction with Amberlyst-15 using pseudo-second order and Langmuir Hinshelwood Hougen Watson models.

A linear plot of model equation at different temperatures is commonly used to determine the kinetic parameters and activation energy of the LA conversion to ALs. Yadav and Yadav [90] implemented the pseudo-first order kinetic model to determine the kinetic parameters of the reaction, while an activation energy of 37.7 kJ/mol was obtained through the Arrhenius plot. Similar kinetic model was applied for LA esterification reaction with ethanol in the presence of carbon cryogel from lignin-furfural [91] and ionic liquid-furfural [92]. Kinetic models (Eqs. 3 and 4) were developed from the rate of reaction equations (Eqs. 1 and 2). The selection of kinetic model was made based on the linearity of the plotted data with support of the parity plot between experimental and predicted data. Both catalysts demonstrated low activation energy, proving the ability of the carbon-based catalysts in this reaction. Moreover, the reaction was also categorized under the kinetic regime.

where, C_A, C_B, C_C, and C_D are the concentrations of LA, ethanol, EL, and water respectively, meanwhile, α, β, γ, and δ are their respective reaction order. k_1 and k_2 are the kinetic constants for the forward and reverse reactions. The assumptions while utilizing the equation are excess ethanol was used (C_B^{β} = constant) and the reaction is irreversible ($k_1 \gg k_2$). Hence, the kinetic model can be simplified to Eqs. (3) and (4).

$$-\frac{dC_A}{dt} = k_1 C_A^{\alpha} C_B^{\beta}$$ Equation 3

$$-\frac{dC_A}{dt} = k C_A^{\alpha}$$ Equation 4

where, $k = k_1 C_B^{\beta}$ is a constant.

$$Levulinic\ acid\ (C_A) + Ethanol\ (C_B)\ k_1\ k_2^{\leftrightarrow}\ Ethyl\ levulinate, C_C + Water, C_D$$ Equation 1

$$-r_A = -\frac{dC_A}{dt} = k_1 C_A^{\alpha} C_B^{\beta} - k_2 C_C^{\gamma} C_D^{\delta}$$ Equation 2

Table 3. Kinetic models for catalytic LA conversion to ALs and its respective activation energy

Catalyst	ALs	Kinetic model	Reaction condition	E_a (kJ/mol)	Ref.
Micro/meso HZ-5	ML	Pseudo-second order	90-130 °C	51.6	[86]
Micro/meso HZ-5	EL	Pseudo-second order	90-130 °C	27.4	[86]
Desilicated HZSM-5	EL	Pseudo-second order	90-130 °C	21.1	[87]
DPTA/DH-ZSM-5	EL	Pseudo-second order	76-84 °C	29.4	[88]
Mesoporous super acidic zirconia	EL	Pseudo-first order	140-170 °C	37.7	[90]
Carbon cryogel lignin furfural	EL	Pseudo-first order	78-150 °C	20.2	[91]
Ionic liquid-furfural carbon	EL	Pseudo-first order	78-170 °C	17.3	[92]
Amberlyst-15	BL	Pseudo-second order	87-127 °C	34.9	[89]
Amberlyst-15	BL	Langmuir Hinshelwood Hougen Watson	87-127 °C	39.9	[89]
Micro/meso HZ-5	BL	Pseudo-second order	90-130 °C	21.3	[86]
Micro/meso HZ-5	OL	Pseudo-second order	90-130 °C	17.1	[86]

The thermodynamic parameter is commonly determined using the Eyring equation, which can be also used to describe the relationship of the reaction rate with temperature as explained by the Arrhenius equation. For instance, [91] employed the Eyring equation (Eqs. 5, 6, 7, and 8) with the combination of theory of activated completer on carbon cryogel catalyst which yielded an enthalpy of activation of 17 kJ/mol (endothermic process), entropy of activation of -278 J/mol.K (less disordered system), and Gibbs free energy of activation of 124.1 kJ/mol (endergonic and non-spontaneous reaction). Similar output was observed by [93] and [92] in their thermodynamic studies. A positive value of enthalpy indicates that the reaction is endothermic as energy or heat is adsorbed for the conversion reaction. At the transition state, the formation of reaction intermediates (LA and alcohol) demonstrated a more ordered state compared to the reactants at the ground state. Moreover, a positive Gibbs free energy of activation discloses that the intermediates at the transition state possess a higher energy level as compared to the reactants at the initial state. Badgujar and Bhanage [94] had also reported negative entropy value and positive Gibbs free energy value for the LA conversion to ALs.

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \qquad \text{Equation 5}$$

$$k = \frac{k k_B T}{h} + e\frac{\Delta G^{\ddagger}}{RT} \qquad \text{Equation 6}$$

$$ln\, ln\, \frac{k}{T} = \frac{\Delta H^{\ddagger}}{RT} + ln\frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R} \qquad \text{Equation 7}$$

$$\Delta G^{\ddagger} = -RT\, ln\left(\frac{kh}{k_B T}\right) \qquad \text{Equation 8}$$

where, $\Delta G^{\ddagger}$ is the Gibbs energy of activation, $\Delta S^{\ddagger}$ is the entropy of activation, $\Delta H^{\ddagger}$ is the enthalpy of activation, $K^{\ddagger}$ is the thermodynamic equilibrium constant, R is a gas constant, k is the rate constant, K is the transmission factor, h is Planck's constant, k_B is Boltzmann's constant, T is the absolute temperature, and notation ‡ is the state of activated complex.

As for mechanism study, the reaction conversion of LA to ALs (esterification reaction) is commonly related with the nucleophilic substitution reaction. This proposed mechanism has been reported by previous researches for LA conversion to ALs in the presence of HPW/Zr catalyst [19], silica-included HPA [95], $H_3PW_{12}O_{40}/ZrO_2$–Si(Ph)Si-1.0 [96], and WO_3-SBA-16 [97]. Based on the reaction mechanism of LA on the Brønsted acid sites, adsorption occurs on the catalyst sites by the joining with the oxygen of the LA carbonyl group. This situation causes the adjoining carbon atom of carbonyl group to increase the electrophilicity and form protonated levulinic acid intermediate. The nucleophilic attack (oxygen of alcohol as nucleophile) on protonated levulinic acid intermediate has resulted in the formation of oxonium ions [19, 95]. Finally, the reaction involves the deprotonation of former carbonyl oxygen, water elimination, alkyl levulinate formation, and acid sites regeneration for continuous reaction. The reaction mechanism via nucleophilic substitution is more concentrated on the chemical elementary step on the acid sites which lacks physical adsorption step for reaction on solid catalyst. Zainol et al. [92] have studied the adsorption of LA on solid catalyst using different types of mechanism such as Langmuir–Hinshelwood and Eley-Rideal mechanisms. The plausible mechanism is postulated with the combination of nucleophilic substitution and Eley-Rideal mechanisms. However, the authors have mentioned that the adsorption and desorption of the reactants and products can be confirmed by using more experimental data to describe the mechanism in detail. This explains that more studies can be conducted to understand the reaction mechanisms using various types of catalysts.

The fundamental studies including the effect of parameter on reaction synthesis, kinetic and thermosdynamic, and also the mechanism studies are important to understand the reaction behavior in the presence of different types of catalyst, reactants, and conditions (temperature, pressure, etc.). The findings of these fundamental studies are relevant to be used for future up-scaling works and reactor designing process on ALs synthesis. This information can be also implemented to investigate the separation of product mixture to obtain main products of high purity.

4.0. Future Perspective

ALs are highly advantageous in a wide range of industrial applications. ALs impose less negative environmental effects compared to conventional fossil fuels, as they are potentially derived from biomass chemical derivatives. Regarding the application of catalyst, carbon-based catalysts have demonstrated their capability as a support for the modification of the reaction to yield superior acid catalyst properties. Different modification alternatives can be conducted on various carbon materials to prepare solid acid catalyst and study its potential toward this reaction conversion. The application of carbon-based catalyst is suitable for this reaction due to the low to moderate temperature application (e.g. 60 to 250 ºC), where the degradation of carbon materials can be avoided owing to their high thermal stability. Metal organic framework (MOF) has shown its ability as an excellent catalyst in various applications and a competent candidate for the production of carbonaceous material (e.g. MOF-derived porous carbon) due to its large porosity, adjustable functional group, consistent pore size, and structured characteristics [98]. MOF is a combination of organic and inorganic compounds made up from metal ions and organic ligands (phosphonate, carboxylate, and sulfonated groups) [43]. Commonly, classical solvothermal method is applied in the production of MOF, but recently other methods such as ultrasonic irradiation, microwave irradiation, solvent free method, and electrochemical method are also applied to synthesize MOF [99]. MOF can be utilized as a carbon precursor by direct carbonization of organic ligands (MOF as carbon source) or porous structure of MOF is introduced by organic substance as the carbon source [100]. There is a high potential of this MOF-derived porous carbon to be applied in this reaction to obtain high product yield.

Apart of thermal conversion process to synthesize ALs, an implementation of emerging technologies such as microwave-assisted process is also feasible for this reaction. A non-catalytic reaction of levulinic esterification with ethanol via microwave irradiation was conducted at various reaction conditions [101]. The study results disclosed that the esterification via microwave irradiation yielded a better performance than the conventional heating method. Carbon materials have been extensively used as catalysts (also known as microwave adsorber in certain reaction) for reaction process in microwave. Carbon materials without any active site (e.g., metal) can be utilized to enhance the reaction using microwave. For example, non-metal activated carbon was used for the conversion of furfuryl alcohol to ML using microwave which resulted in 62% of product yield [102]. Besides, this process consumed 100% feed for conversion to various products but mainly methyl levulinate. This study shows the effect of microwave irradiation in substantially accelerating the reaction rate and the potential of carbon-based materials in microwave reaction system.

The microwave technology has begun to expand its applicability including in the esterification synthesis of LA. Ahmad et al. [103] has observed the effects of microwave heating techniques on the synthesis of EL from LA in the presence of silicotungstic acid catalyst. An increased LA conversion in the microwave reactor was discovered due to more efficient heat transmission into the reaction mixture via direct microwave heating as compared to conventional heating reactors. Microwave-assisted esterification of LA with ethanol using p-sulfonic acid calix[4]arene (CX_4SO_3H) organocatalyst was also utilized to synthesize EL [104]. A reaction was conducted at temperature of 80 °C for only 2.5 minutes with 1 mol% CX_4SO_3H catalyst loading to yield >99% of ethyl levulinate conversion. The study highlighted that the microwave-assisted reactions were efficient with short reaction durations, metal and solvent-free, and employed a reusable and non-toxic catalyst. The noncatalytic or catalytic microwave-assisted synthesis is a promising method for preparing ALs toward a green alternative.

ALs have wide potential applications, with fuels additive as the main target application as this chemical could be potentially derived from biomass precursors (non-food feedstock). ALs could be used as oxygenated fuel additives or as blending components in biodiesel [43]. The utilization of lignocellulosic biomass (softwood bark) for the synthesis of ALs by catalytic alcoholysis in methanol with aluminium sulphate catalyst could be favorable for the technical and economic viability of producing ALs, according to the findings by [105]. Currently, ALs blended diesel-biodiesel has been studied as an alternative to improve the fuel properties of biodiesel and engine performance. There are a few research works conducted concerning the fuel properties of ALs blended diesel [106] and the engine performance [107, 108]. More research works should be focused on the fuel properties study and engine performance due the increasing number of research studies on ALs. ALs are potentially applied as additives to diesel-biodiesel as fuel blends. EL and BL were studied to increase the lubricity and conductivity of the diesel fuel [109]. However, due to the low cetane number of both esters and their limited solubility in diesel fuel at low temperatures, some difficulties could raise in the preparation of diesel blended fuel. Previously, the current commercial diesel engine can operate properly when fuelled with EL mixtures containing up to 20% EL [108]. Thus, more study can be conducted to study the fuel properties and performance of ALs blended diesel-biodiesel. It is feasible to employ the ALs to increase the biodiesel-diesel quality for diesel engine performance.

CONCLUSION

The performance of a carbon-based solid acid catalyst is greatly influenced by its total active sites on the surface of the catalyst, which is the most significant factor to the catalytic activity during the esterification reaction. Furthermore, the type of carbon precursor used for carbonization also determines the effectiveness of the catalyst attributed to the carbon content that leads to the formation of various porous structures. Sulfonated carbon catalyst is prepared from carbonaceous material derived from numerous carbon precursors including biomass, by anchoring $–SO_3H$ group via sulfonation. The carbonization and sulfonation must be carefully conducted at optimal conditions for the synthesis of top-notch catalyst. Additionally, carbon catalysts derived from biomass are highly potential to be used industrially since the catalysts are economical, environmentally friendly, renewable as well as easily prepared, stable, and effective for ALs production. The utilization of sulfonated carbon-based catalyst to synthesize sustainable fuel additive should be magnified globally since it is parallel to ‘green technology’ approach. However, the study on the catalyst preparation along with synthesis route of ALs need further improvement to discover more catalysts and process limitations for better production in terms of economic and environmental concerns. As to current progress, numerous research works could be conducted in the future such as the synthesis process which includes ALs from other biomass derivative components, ALs isolation from product mixture, and the implementation of ALs as fuel additive through the properties study and engine performance.

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