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Additional Information

Conversion of Biomass Platform Molecules into Fuel Additives and Liquid Hydrocarbon Fuels

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1. Introduction

The development of new technologies for producing energy and chemicals from sustainable resources has prompted that biomass valorization becomes an important area of research.¹⁻² Biomass provides an ideal alternative to fossil resources; indeed biomass is the only sustainable source of organic compounds and has been proposed as the ideal equivalent to petroleum for the production of fuels and chemicals.

Starch (as well as sugars), triglycerides and lignocellulose are the general classes of feedstocks derived from biomass used for the production of renewable biofuels and chemicals.³ Among them, lignocellulose biomass is the most abundant, and inexpensive nonedible biomass that can be an excellent source of fuels and chemicals without affecting food supplies.

Nowadays, the three main catalytic routes to transform biomass into fuels and chemicals are: gasification, pyrolysis and hydrolysis.^{1, 4} While gasification and pyrolysis deal with whole biomass (lignocellulose) leading to upgradeable platforms such as syn-gas and bio-oil, hydrolysis is a most complicated process that requires that, lignocellulose was broken into its constituents parts. Lignocellulose is composed by lignin (15-20%), which is a methoxylatedphenylpropane three-dimensional structure responsible of the structural rigidity of plants and that surrounds hemicellulose (25- 35%) and cellulose (40-50%). The hemicellulose polymer is formed by C₅ and C₆ sugar monomers such as D-xilose, D-galactose, D-arabinose, D-glucose and D-manose, being xylose the most abundant. From hemicellulose fraction a polymeric xylan is obtained that can be depolymerized to xylose monomer through diluted acid hydrolysis (for instance sulfuric acid). Finally, cellulose is a polymer of glucose units linked by the β -glycosidic bonds. Although is the most abundant plant material resource, its exploitation has been shortened by its composite nature and rigid structure. Most technical approaches to convert lignocellulosic material to chemical and fuels have been focused on an effective pretreatment to liberate the cellulose from lignin composite and break down its rigid structure.⁵ Once isolated cellulose it can be hydrolyzed into glucose monomer under harsher conditions, at elevated temperature and using sulfuric acid as catalyst.

The conversion of these feedstocks into valuable products can be envisaged by subsequent transformations of a set of biomass derivatives molecules, the so-called platform molecules. The selection of these platform molecules was initially performed

by de US Department of Energy (DOE)⁶ in 2004 and revisited recently by Bozell and Petersen⁷ and include sugars (glucose, xylose), polyols (sorbitol, xylitol, glycerol), furans (furfural, 5-hydroxymethylfurfural) and acids (succinic, levulinic, lactic acid). They were selected in base of several indicators such as the availability of commercial technologies for its production and their potential to be simultaneously transformed into fuels and chemicals in a facility so-called biorefinerie.

In contrast to molecules coming from fossil feedstocks, which are essentially unfunctionalized alkanes, platform molecules are already functionalized compounds, what allow transforming them into more valuable chemicals through a lower number of steps than the required when starting from alkanes. However, while biomass is the only source of chemicals alternative to fossil fuels, the production of biofuels from renewable biomass has attracted more attention than the production of chemicals due to the importance of the transportation sector in our society which relies essentially on the non renewable petroleum.

The liquid biofuels most widely used currently are biodiesel and bioethanol. Biodiesel is obtained by transesterification of triglycerides with methanol (or ethanol) while bioethanol is mainly obtained from edible biomass sources such as sugar cane or corn by sugar fermentation processes. However nowadays, an important effort is being done in order to obtain bioethanol from sugars coming from nonedible lignocellulosic biomass.⁸⁻¹⁰ In the last years the consumption of these biofuels has increased exponentially¹¹ due mainly to their production is based on simple and well-known technologies and their partial compatibility with existing transportation infrastructure of gasoline and diesel. However these biofuels possess several drawbacks that limit their use as transportation fuels.¹²⁻¹³ For instance, the low oxidation stability, the corrosive nature and poor cold flow properties of biodiesel have been considered a disadvantage. Bioethanol is also slightly corrosive and it has to be used blended with gasoline inducing water absorption in the fuel, increasing then the risk of engine damages. These limitations have motivated the search for new approaches for the production of high energy density biofuels (advanced biofuels) compatible with the present transportation infrastructure.

Catalytic transformation of platform molecules into liquid hydrocarbon fuels appears as an interesting approach for the production of advanced biofuels. However, platform

molecules are highly oxygenated compounds and their conversion into liquid hydrocarbon fuels requires oxygen removal reactions (i.e. dehydration, hydrogenolysis, hydrogenation, decarbonylation/decarboxylation, etc.) and in some cases in combination with the adjustment of the molecular weight via C-C coupling reactions (e.g aldol-condensation, ketonization, oligomerization) of reactive intermediates. These C-C coupling reactions are especially important when starting from biomass derivatives with C₅-C₆ carbons (derived from monosaccharides) and the final products are hydrocarbon fuels to be used in diesel engines (C₁₀-C₂₀) and jets (C₉-C₁₆).

Another interesting use of platform molecules in the field of renewable biofuels is their transformation into fuel additives. In general, a fuel additive (gasoline/diesel additive) is a chemical compound that is added to fuels in order to accomplish a variety of functions such as helping to maintain the cleanliness engine part, temper fuel gelling and nozzle choking, prevent corrosion and incomplete combustion of the fuel, improve fuel economy and reduce greenhouse gas and particulate emissions¹⁴. Since the introduction of reformulated and oxygenated gasoline in 1990, an important research on fuel additives has been developed in order to meet the ever more severe emission specifications of vapor pressure, sulfur, olefins, soot and smog reduction¹⁵.

Thus, the transformation of platform molecules into hydrocarbon biofuels or fuel additives is cost competitive with petrochemical technologies and for that is required the development of new approaches that simplify processing by reducing the number of reactions, purification and isolation processes.

A variety of processes for the production of liquid hydrocarbon fuels and fuel additives derived from biomass feedstock have been developed in the last years which will be discussed in this work. In Chart 1 are displayed the main routes to obtain liquid transportation fuels and fuel additives starting from platform molecules.

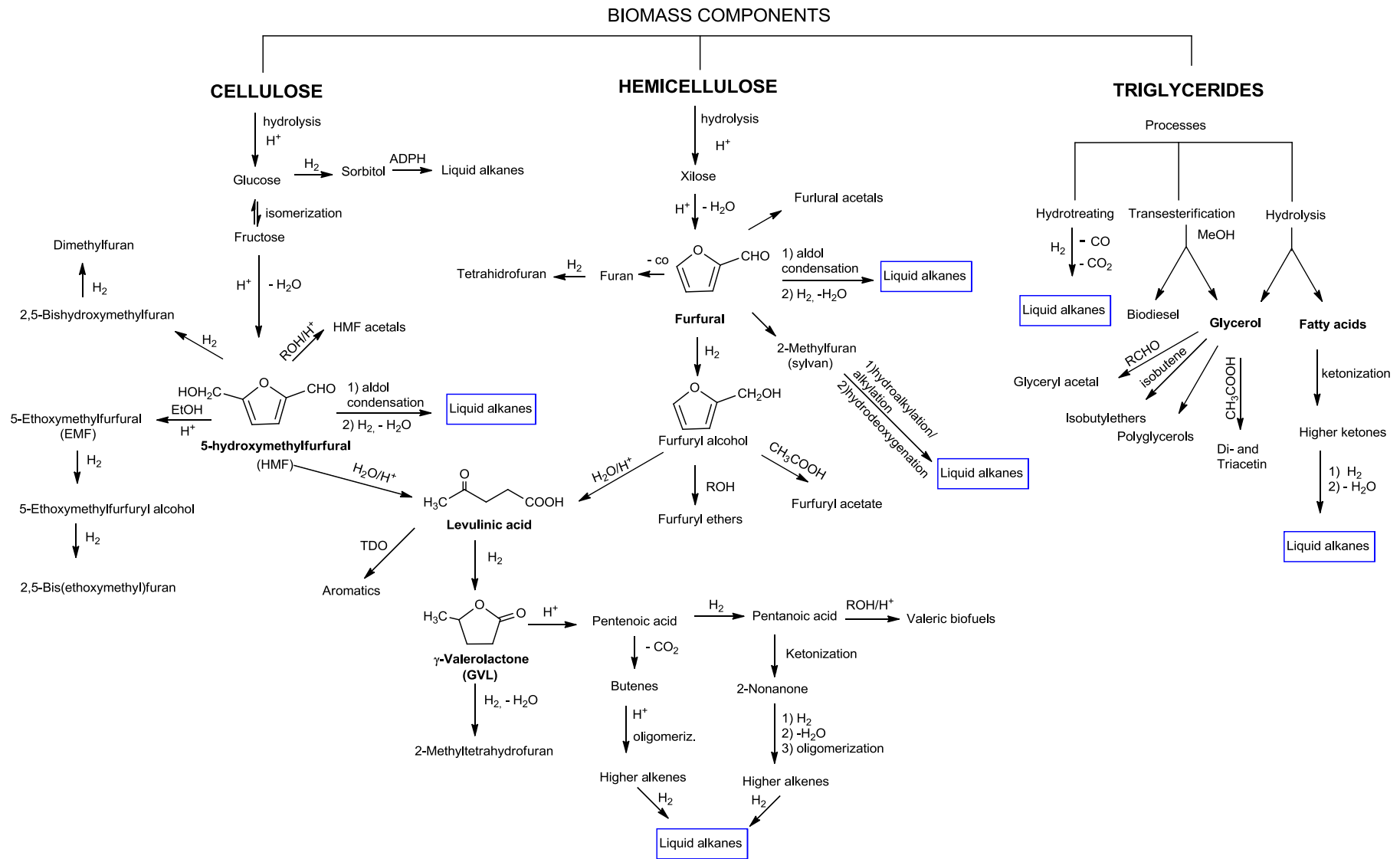
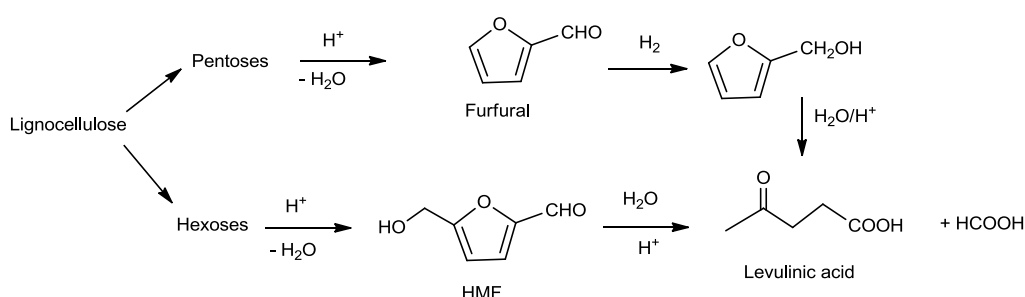


Chart 1. Processing options to convert biomass into valuable fuels and fuel additives

2. Levulinic acid as platform for fuel additives and liquid hydrocarbon fuels

Levulinic acid (4-oxopentanoic acid) can be considered as one of the most important compounds in the selected list of platform molecules derived from biomass⁷ due to its reactive nature along with the fact that it can be produced from lignocelluloses wastes at low cost.

Levulinic acid is formed by dehydration in acidic media of hexoses to HMF which subsequent hydration produces levulinic acid, equimolar amounts of formic acid along with large amounts of humic acids or humins, black insoluble materials, which are produced by unwanted polymerization reactions.¹⁶ Additionally, pentoses such as xylose, the main component of the hemicellulose fraction, can be converted to levulinic acid. In this case the process involves the dehydration of xylose to furfural, subsequent hydrogenation to furfuryl alcohol which is finally hydrolyzed to levulinic acid (Scheme 1).



Scheme 1. Production of levulinic acid from lignocellulose

At industrial scale, Levulinic acid is produced by acid treatment (usually with strong homogeneous acids such as H₂SO₄ and HCl) of lignocellulose. Among the different processes developed for the large-scale continuous production of levulinic acid, one of the most promising approach is the Biofine process.¹⁷⁻¹⁸ In this process the lignocellulose is mixed with sulphuric acid (1.5-3 wt %) and supplied continuously to a first reactor at 488 K and 25 bar during 12 seconds to minimize degradation reactions. The hydrolysis produces HMF which is removed continuously from the first reactor and supplied to a second reactor where it is submitted to a temperature of 466 K and 14 bar during 20 min, producing levulinic acid in yields between 70-80 % of the theoretical maximum, and correspond to 50 % yield based on the hexose content of the cellulosic material. Furfural arising from dehydration of pentoses as well as formic acid are

condensed and separately collected, while solid humins are removed from the levulinic acid and burned to produce heat and electricity. The use of inexpensive lignocellulosic wastes (agricultural residues, paper mill sludge, urban waste paper) in the Biofine process allows production of levulinic acid at competitive costs (0.06-0.18 €/Kg) to be used as platform molecule.¹⁹ Thus, due to high functionality of levulinic acid (i.e. a ketone and an acid function) it can be converted in a variety of valuable chemicals^{2, 19-20} as well as in advanced biofuels. In the next sections different processes to upgrade levulinic acid into biofuels will be discussed.

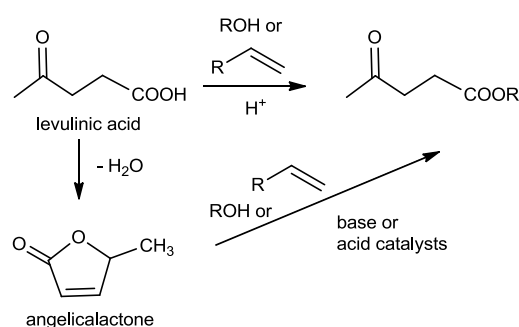
2.1. Levulinic acid as platform for fuel additives

2.1.1. Levulinic acid esters

Levulinate esters are compounds widely used in the food industry, as solvent and plasticizers. Moreover, they also exhibit characteristics that make them appropriate for use as cold flow improver in biodiesel²¹ and as oxygenate additives for gasoline and diesel fuels²²⁻²⁵ such as low toxicity, high lubricity, flash point stability and moderate flow properties under low temperature conditions²⁶. Particularly ethyl and methyl levulinate can be blended with diesel fuel, and studies performed by Biofine and Texaco²⁷ showed that mixtures containing 20% ethyl levulinate, 79% diesel and 1% of other co-additives can be used as fuel with reduced sulfur emissions in Diesel engines.

Levulinate esters can be obtained in good yields through different routes (Scheme 2). One of them is direct esterification of levulinic with alcohols which is typically acid catalyzed by homogeneous catalysts such as sulfuric acid.²⁸ Recently, and as an alternative to extract levulinic acid from aqueous sulfuric feedstocks, levulinate esters have been obtained by reactive extraction with different alcohols²⁹⁻³¹ or with olefins.^{29, 32} A variety of heterogeneous catalysts have also been used for the esterification of levulinic acid with alcohols. For instance methyl and ethyl levulinate have been obtained in 73-76 % yield from levulinic acid and methanol or ethanol using heteropolyacid-silica composites.³³⁻³⁴ Levulinate esters have also been obtained in one-pot process by reacting glucose or fructose with alcohols in the presence of heterogeneous catalysts. Riisager et al.³⁵ reported that on sulphonic acid functionalized SBA-15, 57 % yield of ethyl levulinate can be obtained by reacting fructose and ethanol at 413 K. Starting from glucose or levoglucosan in methanol and using Amberlyst 70 as acid catalyst, >90 % of methyl levulinate could be obtained at temperatures between

423-443 K.³⁶ Levulinate esters can be also obtained directly from cellulosic biomass. For instance, Mascari and Nikitin reported an efficient procedure for converting cellulose into levulinate esters through two reaction steps: biomass reacted with hydrochloric acid followed by esterification with alcohols of the resulting products.³⁷ Tominaga et al.³⁸ used a mixed-acid systems consisting of both Lewis (metal triflate) and Bronsted acids (sulfonic acid) to convert efficiently cellulose into methyl levulinate. It was found that the hydrolysis of cellulose to sugars was mainly catalyzed by Bronsted acids, while the conversion of sugars into methyl levulinate was mainly catalyzed by Lewis acids. In Table 1 are presented recent results on the catalytic preparation of various levulinate esters.



Scheme 2. Different routes to obtain levulinate esters

Table 1. Preparation of levulinate esters with different catalysts

Catalyst	Solvent	Substrate	T(K)	t(h)	Ester Yield (mol%)	Ref
Amberlyst-70	methanol /H ₂ O	levoglucosan	473	3	80	36
SO ₄ ²⁻ /TiO ₂	methanol	glucose	473	2	33	30
SO ₄ ²⁻ /TiO ₂	methanol	fructose	473	2	59	30
SO ₄ ²⁻ /TiO ₂	methanol	sucrose	473	2	43	30
SO ₄ ²⁻ /ZrO ₂	ethanol	glucose	473	3	30	39
SO ₃ H-SBA15	ethanol	fructose	413	24	57	35
40-WD-S ^a	ethanol	levulinic acid	351	10	76	33

DTPA/K10 ^b	butanol	levulinic acid	393	4	97	40
La(OTf) ₃ -2NA	methanol	cellulose	453	5	75	38
C ₅₂ H _{0.5} PW ₁₂ O ₄₀	methanol	cellulose	563	1min	20	41
	/H ₂ O ^c					

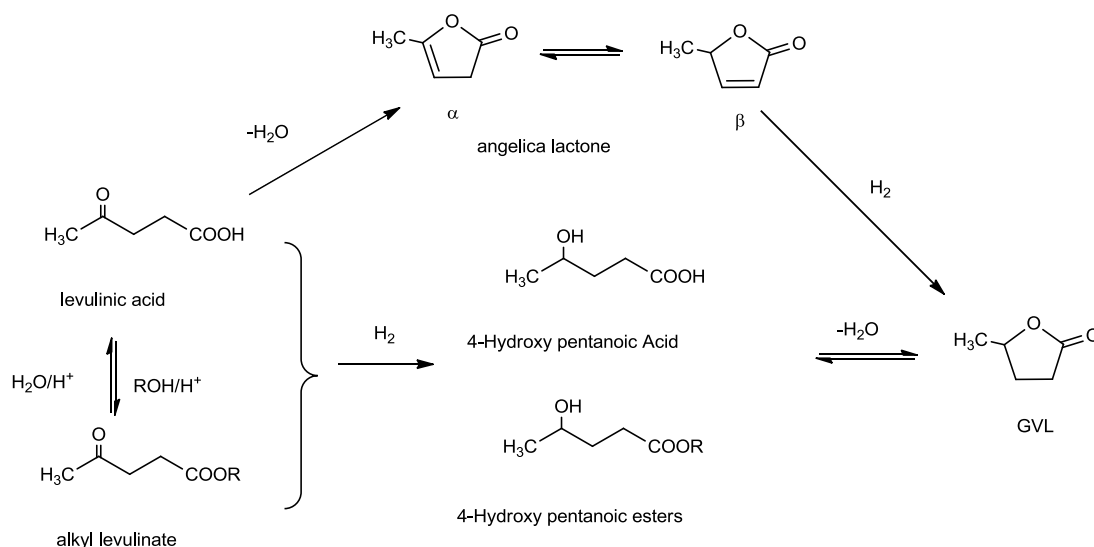
^a40-WD-S: Silica-included Wells-Dawson heteropolyacid; ^bDTPA/K10: dodecatungstophosphoric acid supported on Montmorillonite K10. ^c Supercritical CH₃OH/H₂O (9:1) as reaction media.

A second route is the reaction between angelica lactone with alcohols in the presence of acid or base catalysts,⁴²⁻⁴³ or with alkenes and water using homogeneous or heterogeneous acid catalysts⁴⁴ (Scheme 2). Owing to the presence of water which is stoichiometrically required, levulinic acid is also obtained as byproduct which can be further esterified. Finally, levulinate esters can be obtained by alcoholysis of furfuryl alcohol under acid catalysis. Thus ethanolysis of furfuryl alcohol using acidic resins as catalysts yield 87 % of ethyl levulinate, while acidic zeolites such as H-ZSM-5 gives a lower activity and selectivity with a higher coproduction of diethyl ether.⁴⁵

2.1.2. Reduction of Levulinic acid to Gamma-Valerolactone (GVL)

GVL is a five carbons cyclic ester which have applications for production of perfumes, food additives⁴⁶ and as a solvent as well as a precursor for other green solvents⁴⁷⁻⁴⁸. Additionally, GVL can be used as fuel additive to current fuels derived from petroleum in similar way as ethanol. For instance, Horvath et al.⁴⁶ have compared mixtures of 90 vol% gasoline with 10 vol% ethanol or 10 vol% GVL showing that at similar octane numbers, the mixture with GVL improved the combustion due to its lower vapor pressure. On the other hand, although GVL has not been tested as a pure fuel, it has combustion energy similar to ethanol (35 MJL⁻¹) and a higher energy density which confers to GVL potential to be used directly as a liquid fuel.

GVL can be produced from levulinic acid via two main routes. One of them involves the hydrogenation of levulinic acid (or its ester) to gamma-hydroxyvaleric acid (or ester) which by an intramolecular esterification⁴⁹⁻⁵⁰ produces GVL. A second route, involves the acid catalyzed dehydration of levulinic acid to angelica lactone followed by hydrogenation (Scheme 3), however in this case yields of GVL are lower since acidic media promotes the polymerization of angelica lactone and formation of coke.⁵¹



Scheme 3. Routes for the production of gamma-valerolactone (GVL)

The development of environmentally benign, cost efficient processes for the synthesis of GVL has received extensive attention, and several routes using different catalysts and hydrogen sources for the reduction of levulinic acid have been developed in recent years. Thus, hydrogenation of levulinic acid to GVL has been performed using both heterogeneous and homogeneous metal catalysts at relatively low temperatures (373-543 K) and high pressures (50-150 bars). Ruthenium complexes bearing monodentate phosphorous ligands are the principal catalysts used for homogeneous hydrogenation of levulinic acid. For instance, levulinic acid has been hydrogenated to GVL under relatively mild conditions with $\text{RuCl}_2(\text{PPh}_3)_3$,⁵² $\text{Ru}(\text{acac})_3$ ligated with PBU_3 or tris(3-sulfonatophenyl)phosphine (TPPTS)⁵³ and RuCl_3 combined with TPPTS⁵⁴ or PPh_3 ⁵⁵⁻⁵⁶ in excellent yields (up to 99 %). Nevertheless, the main problem of these catalytic systems for practical use is the low turnover numbers (TONs) which in some cases do not exceed of 1600.⁵³ Recently Li et al.⁵⁷ reported that Iridium trihydride catalyst bearing pyridine-based pincer ligands showed very high activity for levulinic acid hydrogenation to GVL achieving yields between 96-99% and TOFs of 71000, although the presence of strong homogeneous bases such as KOH or NaOH is required in order to achieve high yields of GVL.

The use of solid catalysts for hydrogenation of levulinic acid to GVL has been extensively studied in gas and liquid phase. Recently Wriht and Palkovits⁵⁸ reported an

excellent review on different methods to produce GVL from levulinic acid using mainly heterogeneous catalysts. Therefore, in the present manuscript we briefly illustrate a few recent relevant examples to produce GVL from levulinic acid.

Reduction of levulinic acid to GVL using external H₂, has been typically performed using metal catalyst such as Ru, Pd, Pt, Ni, Rh, Ir, Au on different supports with variable success. Among them, Ru catalysts shown high performance to reduce levulinic acid or its esters⁵⁹ to GVL. Thus, Manzer⁶⁰ showed that GVL can be obtained with 97 % yield by hydrogenation of levulinic acid in dioxane as a solvent at 423 K with 5 wt% Ru/C, while 99 % yield could be obtained in a continuous process in supercritical CO₂ over a Ru/SiO₂ catalyst.⁶¹ Selective hydrogenation of levulinic acid to GVL has been efficiently performed with Ru, Pt and Pd supported on carbon under gas phase in a continuous reactor system.⁶² Among the different catalysts, 5 wt% Ru/C gave the highest activity and selectivity to GVL (100% selectivity at 100% LA conversion). The catalyst activity was maintained during 240 h. The higher catalytic activity and selectivity of Ru/C catalyst was attributed to the higher dispersion of nano-metallic Ru particles over carbon compared to Pt and Pd catalysts. Also, Lange et al.⁶³ performed a continuous hydrogenation of levulinic acid with platinum supported on TiO₂ or ZrO₂, affording 95 % yield of GVL with negligible deactivation over 100 h. Additionally, other non noble metals which can reduce the cost of the process have been tested in this transformation. For instance, the hydrogenation of levulinic acid and its esters with Cu/Al₂O₃ and Cu/ZrO₂ in water and methanol respectively afford quantitative hydrogenation of levulinic acid and its methyl ester with 90-100% selectivity to GVL.⁶⁴ While the metal leaching was important for the Cu-Al₂O₃ catalyst in a water medium due to the formation of a copper-carboxylate complex, copper leaching was completely suppressed in the case of the Cu-ZrO₂ catalyst in methanol showing excellent recyclability. From an environmental point of view, it could be more interesting to perform the hydrogenation of levulinic acid in water. This has been achieved⁶⁵ with a Cu catalyst derived from Hydrotalcites. Among different Cu-Hydrotalcites (Cu-Al, Cu-Cr, Cu-Fe), the best performance was found for a Cu-Cr Hydrotalcite (Cu⁺²/Cr⁺³ molar ratio =2), where 91 % yield of GVL at > 99 % conversion of levulinic acid was achieved. In addition, this catalyst showed also good activity to hydrogenate furfural to furfuryl alcohol.

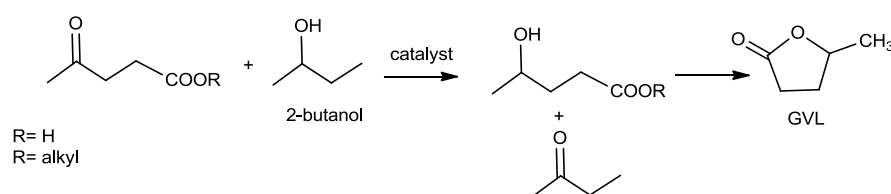
An interesting integrated process for production of GVL involves the *in situ* production of hydrogen by decomposition of the formic acid produced as by-product in the manufacture of levulinic acid,^{29, 53, 55, 66-70} being Ru based catalysts the most commonly used. It is interesting to point out that in some cases the same catalysts used for hydrogenation of levulinic acid to GVL, are also active to catalyze the decomposition of formic acid. Thus, Deng et al. have reported the synthesis of GVL in 96 % yield using homogeneous⁵⁵ and heterogeneous⁶⁶ Ru based catalysts using the above strategy. This process does not require the need for external H₂ and eliminates the need of previous purification of levulinic acid for its hydrogenation to GVL. In fact, it has been observed that the presence of impurities and mineral acids present in the feed of levulinic acid deactivate the catalyst decreasing considerably the yields of GVL.⁷¹ The hydrogen transfer mechanism in this process is not clear yet, and two possible routes have been proposed. One of them involves formic acid decomposition into H₂ and CO₂, being H₂ the reducing agent. A second possible mechanism claims that a metal-formate is formed during the reaction which decomposes into CO₂ and a metal-hydride that reduces levulinic acid to GVL.⁵⁵

As commented above, production of GVL from aqueous solutions containing levulinic and formic acids along with mineral acids such H₂SO₄, is challenging due to the deactivation of the hydrogenation metal catalysts. To minimize this problem, different systems for extracting levulinic acid from the acid aqueous solutions, have been proposed. For instance, it has been reported that alkylphenol solvents are able to extract up to 80 % of levulinic acid from these aqueous feedstocks.⁷² Also, the reactive extraction with different alcohols²⁹⁻³¹ or with olefins^{29, 32} to produce levulinate esters which can be easily separated from the aqueous feedstock have been proposed. These extracting systems allow obtaining levulinic acid pure enough to be hydrogenated to GVLn and the recycle of the mineral acid. Another alternative is the use of acid-resistant catalysts. For instance, Braden et al.⁷¹ have showed that ReRu/C is more stable than Ru/C although comparatively, the TOF of the former was still low.

Direct synthesis of GVL from carbohydrates (fructose, glucose, sucrose, cellulose) through a one-pot process involving hydrolysis/dehydration of the carbohydrate to form levulinic acid which is subsequently hydrogenated to GVL has been recently reported.^{55, 67} Starting from fructose and using an homogeneous acid catalyst such as trifluoroacetic acid in combination with Ru/C and formic acid as a

source of hydrogen, the highest yield of GVL (52 %) was obtained at 453K after 16 h reaction.⁶⁷ Humins were the major by-products formed during the acid catalysed conversion of D-fructose to the intermediate levulinic acid. However, using molecular hydrogen (94 bars) the highest yield of GVL (62 mol%) was obtained after 8 h at complete conversion of D-fructose. Under these reaction conditions, lower yields of GVL were obtained starting from sucrose (52%), glucose (38%) and cellulose (29%), which is in good agreement with the lower conversion of these carbohydrates into levulinic acid in acidic media reported in literature (46 % for glucose,⁶⁰ 40 % for sucrose⁵³ and 29 % for cellulose⁷³)

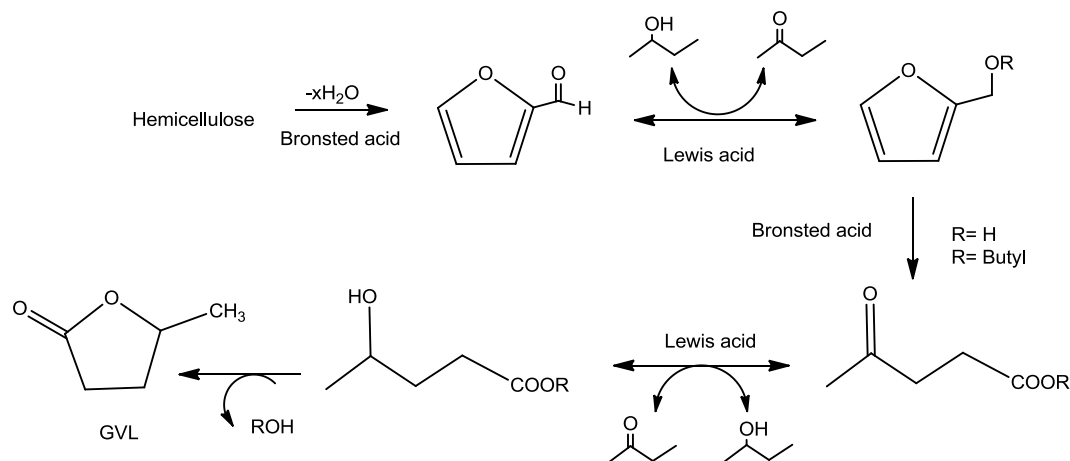
Finally, an alternative route to produce GVL from levulinic acid which not requires the use of expensive noble metal catalysts is the transfer hydrogenation of levulinic acid through the Meerwein-Ponndorf-Verley reaction using secondary alcohols as hydrogen donor (Scheme 4). Chia et al.⁷⁴ performed the hydrogenation of levulinic acid and its esters to GVL using secondary alcohols as hydrogen donor and solvent in the presence of different metal oxides, such as ZrO_2 , MgO/Al_2O_3 , MgO/ZrO_2 , $CeZrO_x$ and $\gamma-Al_2O_3$. The highest yield to GVL (92%) was achieved with ZrO_2 working at 423 K, and 2-butanol as a source of hydrogen. Although fast catalyst deactivation was observed, catalytic activity could be restored by further calcination of the catalyst in air.



Scheme 4. Hydrogenation of levulinic acid through the Meerwein-Ponndorf-Verley reaction

Transfer hydrogenation reactions have been recently used by Roman-Leshkov et al.⁷⁵ to convert furfural into GVL in one-pot process. Using a combination of solid Lewis and Bronsted acid, the authors performed a sequential process which involves as first step a transfer hydrogenation with 2-butanol of furfural into furfuryl alcohol and butyl furfuryl ether promoted by a Lewis acid catalyst. Next, a Bronsted acid catalyst promotes the hydrolytic cleavage of the furanic C-O bond giving a mixture of levulinic acid and butyl

levulinate which subsequently underwent a second hydrogen transfer reaction to produce the corresponding 4-hydroxypentanoates that lactonize to GVL (see Scheme 5). Under optimized reaction conditions and using Zr-Beta zeolite as Lewis acid, and an aluminosilicate with MFI topology and nanosheet morphology (Al-MFI-ns) as Bronsted acid catalyst, 78 % yield of GVL was obtained.

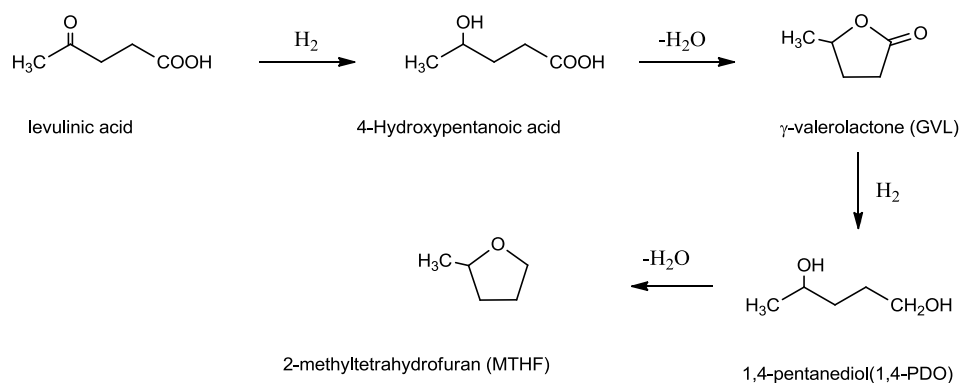


Scheme 5. Domino reaction for the production of GVL from hemicelluloses by the use of a combination of Lewis and Bronsted acids

2.1.3. Reduction of Levulinic acid to Methyltetrahydrofuran (MTHF)

MTHF is a hydrophobic compound which can be blended up to 60%(v/v) with gasoline and used in current internal combustion engines without adverse effects on engine performances. Compared with gasoline, MTHF possesses lower heating value; however this disadvantage is compensated by a higher specific density, which gives similar mileage that gasoline. MTHF has been identified as one of the components of the so-called P-series fuels which are approved by the US DOE for use in gasoline vehicles.

MTHF can be produced by catalytic hydrogenation of levulinic acid over homogeneous and heterogeneous metal catalysts, however this process can generate different compounds depending on the catalyst and reaction conditions. The general pathways of reduction are presented in Scheme 6. Levulinic acid is hydrogenated to 4-hydroxypentanoic acid which spontaneously dehydrates to GVL. This is hydrogenated to 1,4-pentanediol (PDO) which dehydrates to 2-methyltetrahydrofuran (MTHF), giving pentanoic acid and pentanol as side products.



Scheme 6. General pathways of reduction of levulinic acid into MTHF

The US Pacific Northwest National Laboratory, patented in 1998 a process able to produce high yields of MTHF from levulinic acid⁷⁶ using a bifunctional PdRe/C catalyst. The catalyst is able to convert levulinic acid at 473- 523 K and 100 bar of H₂ into MTHF, in a single process vessel with yields up to 90 %. More recently, direct hydrocyclization of levulinic acid to MTHF over Nanocomposite Cu/SiO₂ catalysts in vapor phase and at moderate H₂ pressures (25 bar) has been reported by Upare et al.⁷⁷ The authors showed that the selectivity to GVL, or MTHF can be tuned by the metal loading. Thus, 5wt % Cu/SiO₂ promotes mainly the hydrogenation of levulinic acid to GVL (99.9 % yield), while increasing the Cu loading up to 80%, MTHF and 1-pentanol were obtained in 64% and 35 % yield respectively. Additionally it was showed that the addition of Ni to this catalyst enhanced the selectivity to MTHF (89 %) without significant loss of catalytic activity for 320 h. Tunable direct conversion of GVL to MTHF or 1,4-PDO can be achieved by using Cu/ZrO₂ catalyst.⁷⁸ When the Cu catalyst was calcined in presence of air, and working at 513 K, 60 bar of H₂ in presence of ethanol, GVL was converted to MTHF with 93% selectivity at 98 % GVL conversion. However, when the catalyst was calcined in presence of H₂ and the reaction temperature was decreased at 473 K, 98 % yield of 1,4-PDO was obtained. Homogeneous catalysts have been also used to reduce levulinic acid to MTHF with excellent performances. Geilen and coworkers⁷⁹ performed the hydrogenation of levulinic acid using ruthenium complexes, showing that the selectivity can be tuned to MTHF, GVL or 1,4-PDO depending on the nature of ligands and additives (see Table 2). Thus, 1,4-PDO was obtained in 95 % yield with triphos as ligand, however upon addition of an acidic ionic liquid the selectivity was shifted to MTHF (92 % yield). Interestingly, these catalytic systems were applied to the reduction of itaconic acid which gives 3-

methyltetrahydrofuran. Results showed that using Ru-triphos catalyst in the presence of NH_4PF_6 and p-toluenesulfonic acid as additives, itaconic acid could be reduced to 3-MTHF in 97 % yield.

Table 2. Influence of the ligand, additive and reaction temperature on the Ru-catalyzed conversion of levulinic acid.^a (adapted from ref⁷⁹)

Ligand	T (K)	Additive	GVL	1,4-PDO	MTHF	others ^c
PnOct ₃	433	NH_4PF_6	>99	0	0	0
dppb	433	NH_4PF_6	89	30	3	11
triphos	473	NH_4PF_6	7	31	59	3
triphos	433	-	3	95	0	2
triphos	433	aIL ^b	5	1	87	7
triphos	433	aIL ^b + NH_4PF_6	1	0	92	7

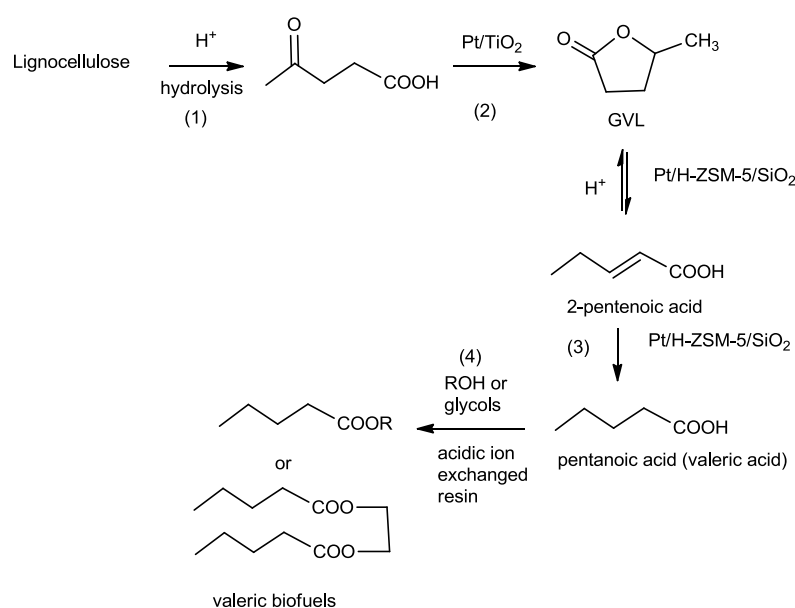
^a Conditions: 10mmol LA, 01 mol% $[\text{Ru}(\text{acac})_2]$, 1.0 mol% PnOct₃(trioctylphosphine), 0.3 mol% dppb(1,4-diphenylphosphinobutane) or 0.2 mol% triphos(1,1,1-tris(diphenylphosphinomethyl)ethane, 1 mol% additive, reaction time 18 h, H_2 10MPa. ^b acidic ionic liquid ((4-sulfobutyl)imidazolium-p-toluenesulfonate). ^c monoalcohols, mainly 1-pentanol. Full conversion of LA was achieved in all cases.

Additionally, MTHF can be converted into hydrocarbon fuels. The hydrogenolysis of MTHF at high pressures of H_2 and moderate temperatures in the presence of $\text{Pt}(\text{acac})_2$ in $\text{CF}_3\text{SO}_3\text{H}$ results in a mixture of alkanes (C4-C9 alkanes).⁵³

2.1.4. Hydrogenation of Levulinic acid to alkyl pentanoic esters (Valeric biofuels)

A new platform of levulinic acid derivatives, alkyl valerate esters (valeric biofuels) were produced by Lange et al.⁶³. The synthesis of valeric biofuels involves the acid hydrolysis of lignocellulose materials to levulinic acid, the hydrogenation of the acid to GVL, the hydrogenation of GVL to valeric acid and its subsequent esterification with alcohols or glycols to alkyl valerate esters (Scheme 7). The formation of valeric acid from GVL, is believed to start with the acid catalyzed ring-opening of GVL to pentenoic acid and subsequent hydrogenation to valeric acid (Scheme 7). The process is performed over a bifunctional acid-metal catalyst which requires an optimal balance of

the acid and hydrogenation functions. Among ~150 catalysts evaluated in a continuous high-pressure plug-flow reactor, Pt-loaded SiO₂-bound H-ZSM-5 was identified as a very effective catalyst, achieving valeric acid yields over 90% yield. This performance was maintained for more than 1500 h only requiring intermittent catalyst regeneration by calcinations in air. The esterification of valeric acid with different alcohols was performed using acidic ion-exchange resins achieving above 95 % selectivity to the corresponding esters. In Table 3 are presented the key performance factors for the individual process steps.



Scheme 7. Pathways of transformation of lignocellulose into valeric biofuels

Table 3. Key performance factors for individual process steps presented in Scheme 7

Catalysts	Step-1 Hydrolysis	Step-2 Hydrogenation	Step-3 Hydrogenation	Step-4 Esterification
Catalyst	H ₂ SO ₄	Pt/TiO ₂	Pt/ZSM-5	Acidic resin
Selectivity	50-60%	>95%	>90%	>95%
Productivity	>01 h ⁻¹	>10 h ⁻¹	>1 h ⁻¹	>0.02 h ⁻¹
Concentration	<5%	>90%	>50%	>50%

Selectivity (% mol); productivity ($t_{\text{product}} \text{ m}^{-3} \text{ reactor h}^{-1}$); concentration (wt%). Reaction conditions: Step-2, 40 bar H₂ at 473K; Step-3, 10 bar H₂ at 523 K.

Furthermore, the authors showed that GVL could be directly converted into pentyl valerate (20-50 % selectivity) using Pt/TiO₂ or Pd/TiO₂ catalysts at 548-573 K. The study of the fuel properties of alkyl valerates showed that they have acceptable energy densities and more appropriate polarity than other biofuels such as ethanol, butanol, ethyl valerate, GVL and MTHF. Depending on their alkyl chain length they can be blended with gasoline and diesel fuels up to high blend ratios. For instance, blends of regular gasoline with ethyl valerate at 10 and 20 % vol, possess research (RON) and motor octane number (MON) which meets the specification for European gasoline.

Serrano-Ruiz et al.^{69, 80} reported a similar strategy to convert GVL into pentanoic acid using a series of Pd/Nb₂O₅ catalysts. They found that reaction conditions (Pd loading, temperature, partial hydrogen pressure and WHSV) had strong influence on the catalytic performances. The highest yield to pentanoic acid (92%) was obtained with 0.1 wt% Pd/Nb₂O₅ catalyst and working with a 50wt% aqueous feed of GVL, at 598 K and hydrogen diluted in helium (50:50). Comparatively, Pd/Nb₂O₅ doped with CeO₂ (Pd-NbCe)⁸¹ showed poor conversion, a third of that Pd/Nb₂O₅, which was attributed to a severe decrease in the strength of acid sites upon ceria addition. However, surface acidity could be enhanced by dispersing the active phases over carbon support (Pt-NbCe-C) and near 90 % selectivity to pentanoic acid at 90 % conversion of GVL was achieved which was maintained during 200 h on stream. More recently, Chan-Thaw et al.⁸² reported the production of pentyl and ethyl valerate from GVL in a one-pot process using Cu supported on SiO₂-ZrO₂ and pentanol or ethanol as solvent. Using pentanol, conversions > 90% of GVL and selectivities of pentyl valerate up to 83 % were achieved. The reaction takes place under H₂ through nucleophilic addition of the alcohol to the carboxylic group giving hydroxypentanoate, followed by dehydration to pentenoate and hydrogenation to pentyl valerate. When ethanol was used, ethyl valerate was formed at lower selectivities due to the formation of ethyl 4-ethoxy pentanoate and pentenoic esters.

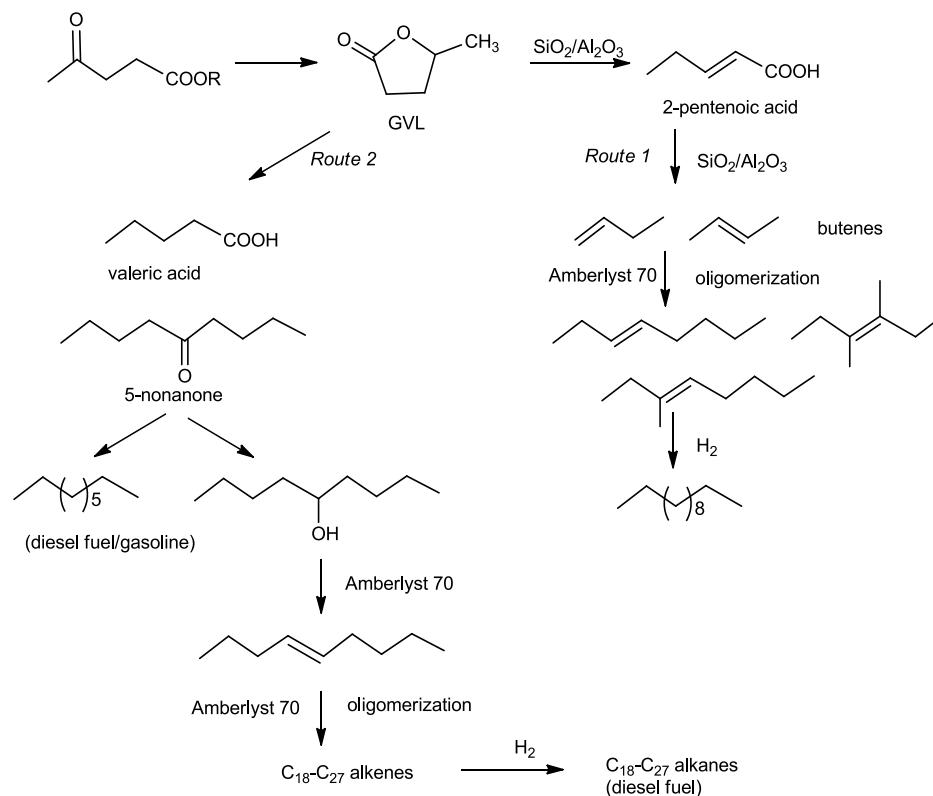
2.2. Levulinic acid as platform for liquid hydrocarbon fuels

Levulinic acid can be transformed to hydrocarbon fuels by a number of catalytic routes involving deoxygenation reactions combined with C-C coupling reactions. As showed above, levulinic acid can be converted in GVL which is the starting material to produce both pentenoic and pentanoic acids, which are more deoxygenated compounds

that levulinic acid. Upgrading levulinic acid to liquid hydrocarbon fuels follows two possible routes. One of them (Scheme 8, route 1) is the production of butenes from pentenoic acid which can be subsequently oligomerized to higher alkenes.⁸³⁻⁸⁵ Bond et al.⁸³⁻⁸⁴ reported the production of liquid hydrocarbon fuels from aqueous solutions of GVL without need for external hydrogen using a dual reactor system. In the first catalytic reactor GVL feed undergoes ring opening to pentenoic acid isomers with subsequent decarboxylation over a $\text{SiO}_2/\text{Al}_2\text{O}_3$ catalyst at 36 bar and temperatures between 498-648 K producing an equimolar mixture of butenes (over 99 % yield) and CO_2 . In a second reactor connected in series the oligomerization of butenes takes place over an acidic catalyst (HZSM-5, Amberlyst 70) to form a distribution of alkenes centered at C_{12} that can be used as jet fuel upon hydrogenation. Particularly Amberlyst 70 resulted an active catalyst for oligomerization of butenes at relatively low temperatures (423 K), this characteristic minimizes the production of undesired cracking products, increasing the selectivity to higher alkenes. Combination of $\text{SiO}_2/\text{Al}_2\text{O}_3$ for decarboxylation of GVL with Amberlyst 70 catalyst for olefin oligomerization it was possible to achieve an overall yield of higher liquid alkenes over 75 %.

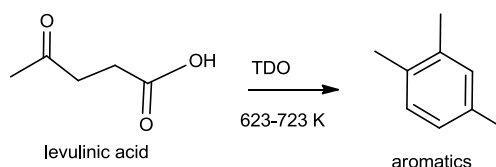
Another route to upgrade (Scheme 8, route 2) levulinic acid to liquid alkanes is via production of pentanoic acid through ring-opening/hydrogenation of GVL on a bifunctional (acid-metal) catalyst as described above. Ketonization of two molecules of pentanoic acid yield 5-nonanone along with CO_2 and water. Serrano-Ruiz et al.⁶⁹ produced 5-nonanone in with high yields (90%) along with lower ketones (2-hexanone and 3-heptanone) from aqueous GVL in a single reactor by using a dual catalyst bed of 0.1%Pd/ Nb_2O_5 (to produce pentanoic acid) plus ceria-zirconia (to produce the ketonization). 5-nonanone product is hydrophobic and separates spontaneously from water, being obtained in high purity. 5-nonanone can be upgraded to liquid alkanes, through its hydrogenation/dehydration to *n*-nonane using a bifunctional catalyst such as Pt/ Nb_2O_5 at 60 bar of H_2 and temperatures between 528-568 K, which possess adequate cetane number to be blended with diesel fuel. Alternatively, 5-nonanone can be hydrogenated to 5-nonanol over Ru/C, at 50 bar and 423 K. The alcohol can be subsequently dehydrated and isomerized over an acid catalyst such as Amberlyst 70 at 423 K to produce nonene which can be subsequently oligomerized to C_{18} alkenes, and hydrogenated to the corresponding alkanes with diesel applications.⁸⁶ Additionally,

lower ketones can also be converted into alkenes, which by further oligomerization with nonene produce C_6 - C_{27} alkenes that can be hydrogenated to alkanes with application as jet fuel or Diesel blenders. Around 50 kg of liquid hydrocarbons can be produced from 100 kg of GVL retaining more than 90% of its energy content through this process.⁸⁶



Scheme 8. Routes for the transformation of levulinic acid into liquid alkanes

Finally, levulinic acid can be converted into aromatic hydrocarbons without using hydrogen by means of thermal deoxygenation (TDO) which is a thermal pyrolysis process (Scheme 9). In this process, levulinic acid is converted firstly in calcium levulinate which is heated at high temperatures (623-723 K) under inert atmosphere at atmospheric pressure.⁸⁷ Under these reaction conditions, calcium levulinate simultaneously ketonizes and deoxygenates (by internal cyclation and dehydration) producing a wide range of aromatic and cyclic compounds (principally cyclic ketones) with low oxygen/carbon ratios which may be candidates for upgrading to hydrocarbon fuels. The quality and yield of TDO products have been recently improved by adding equimolar amounts of calcium formate, which acts as hydrogen source and leads to a highly deoxygenated hydrocarbon oil with an energy density higher than 40MJ/Kg,⁸⁸ and that can be upgraded with the existing hydrocracking technology.



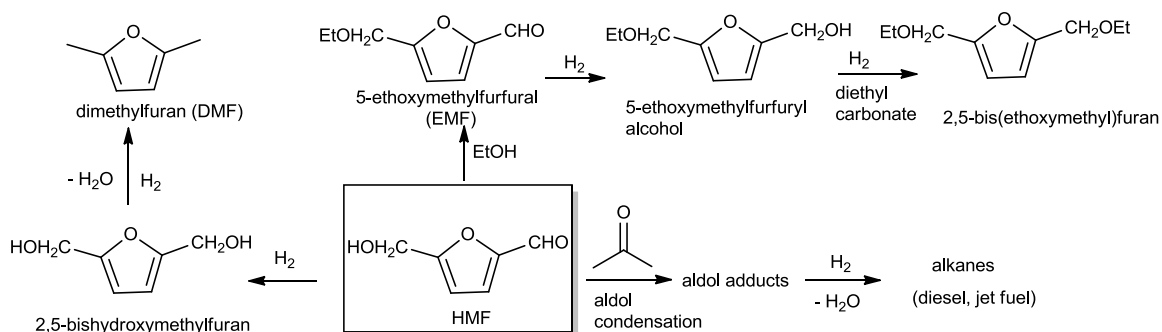
Scheme 9. Thermal deoxygenation of levulinic acid (TDO)

3. Furan derivatives as platform for liquid hydrocarbon fuels and fuel additives

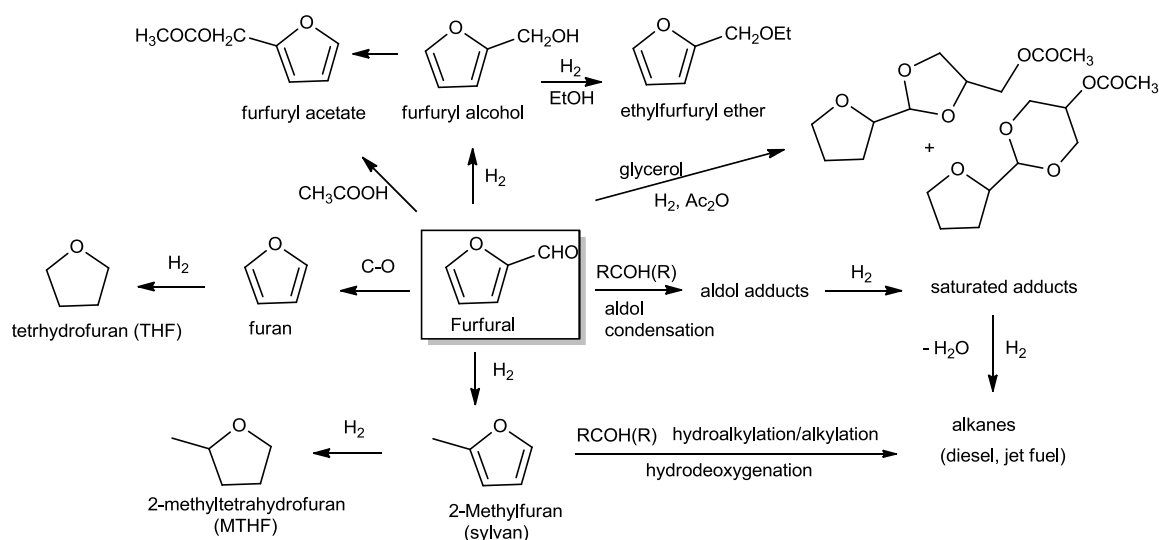
Furfural and 5-hydroxymethylfurfural (HMF) are considered excellent platform molecules which can be converted into fuel additives such as, 2-methylfuran and 2,5-dimethylfuran which are octane boosters, monomers (2,5-hydroxymethylfuran, 2,5-carboxyfuran, etc.) and intermediates for fine chemistry.

Thus, chemical dehydration of hexoses and pentoses allowed to obtain hydroxymethylfurfural (HMF) and furfural (FUR) respectively. Dehydration of sugars to obtain furfural and hydroxymethylfurfural using homogeneous and heterogeneous acid catalysts has been extensively reviewed.⁸⁹⁻⁹¹ Furfural and HMF are not attractive fuel components because of its melting point and stability however they can be used as starting material to produce a variety of high value added furan derivatives,^{1, 92-96} as well as to produce liquid alkanes and fuel additives. In this section we will discuss different strategies to convert furan platform molecules into hydrocarbon liquid fuels and fuel additives.

In Scheme 10 and 11 are summarized different strategies for upgrading HMF and furfural to liquid biofuels respectively, which involve, hydrogenation, deoxygenation, etherification, different C-C formation reactions such as aldol condensation, hydroxyalkylation, alkylation and optional combinations.



Scheme 10. Main routes to transform HMF into fuel additives and liquid alkanes



Scheme 11. Main routes to transform furfural into fuel additives and liquid alkanes

3.1. Furan derivatives as platform molecules for fuel additives

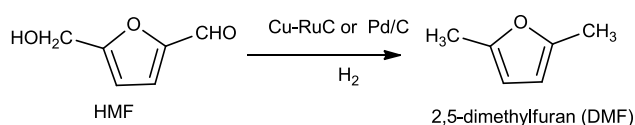
3.1.1. Hydrogenation of furfural and HMF

Hydrogenation is an important reaction to transform HMF and furfural and its derivatives into additives to biofuels. Indeed, the starting molecules have an excessive oxygen content, high reactivity, high solubility in water, high boiling point and low energy density. Thus by selective hydrogenation, HMF can be converted to 2,5-dimethylfuran (DMF) and 5-hydroxymethyltetrahydrofurfural (HMTHDF) depending on the reduction step. Hydrogenation of furfural includes the hydrogenation of carbonyl group to hydroxymethyl or methyl, the hydrogenation of the furan ring and its opening to pentanols, pentane diols and occasionally alkanes. Among them, 2-methyl furan (2-MF) and 2-methyltetrahydrofuran (MTHF) have been reported as fuel components.⁹⁷

3.1.1.1. Hydrogenation of HMF to 2,5-dimethylfuran (DMF)

One of the most attractive furan derivatives as an alternative to gasoline blending is 2,5-dimethylfuran (DMF). DMF has a boiling point of 367 K and an energy content of 31.5 MJ L⁻¹ similar to that of gasoline (35 MJ L⁻¹) and 40% higher than ethanol (23 MJ L⁻¹).⁹⁷ DMF is not soluble in water and can be used as blender in transportation fuels.

The most general method to obtain DMF is by reduction of both the formyl and hydroxyl groups of the HMF using supported metal catalysts in organic solvents such as butanol. Roman-Leshkov et al.⁹⁷ proposed a two step process to obtain DMF in good yields (76-79%). The process consist in the production of HMF starting from fructose (in a biphasic reactor with and acid catalyst) followed by hydrogenation over a carbon supported copper/ruthenium (Cu-Ru/C) catalyst using butanol as solvent (Scheme 12). The same catalyst was also used by Binder et al.⁹⁸ in the hydrogenolysis of crude HMF obtained from corn stover using water as solvent and achieving 49% yield of DMF. Liujsx et al. describes the formation of DMF by hydrogenolysis of HMF in the presence of palladium as catalysts in propanol.⁹⁹ The authors found that the palladium support and the solvent used were process variables of considerable importance which control the final compound obtained. For instance in 1,4-dioxane, 2,5-bis(hydroxymethyl)furan is mainly formed, while in water ring opening becomes a major reaction.



Scheme 12. Catalytic reduction of HMF to dimethylfuran (DMF)

The hydrogenolysis of either neat HMF or HMF obtained by dehydration of glucose using heteropolyacid as catalyst in acetonitrile as cosolvent has been reported.¹⁰⁰ Carbon supported metal catalysts, particularly Pd/C, was effective promoting the hydrogenation of HMF to DMF in EMIMCl (1-ethyl-3-methyl-imidazolium chloride ionic liquid) and acetonitrile as a solvent at 393 K and 62 bar of hydrogen, giving 47% HMF conversion with selectivity to DMF of 32%.

Recently a techno-economic evaluation feasibility of biorefineries based in the production of DMF and HMF from fructose has been published.¹⁰¹ DMF has been obtained starting from HMF in the presence Cu-Ru/C catalyst. The authors claim that the commercial application of DMF as fuel does not seem viable due to the catalytic performance and expensive catalyst used. The result show the price of 1Dolar/Kg of HMF would be a good basis for its use in bulk scale applications as this is the same order of magnitude as current fossil fuel based in raw materials.

Thananattanachon et al.¹⁰² have reported an interesting technology to transform fructose into DMF in one pot in acceptable yield (51%). In the process formic acid, a

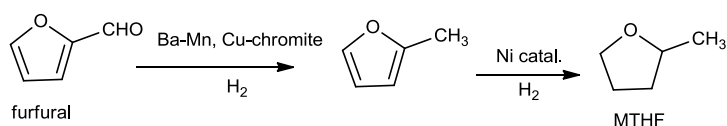
by-product coming from biomass degradation is used as homogeneous acid catalyst to fructose dehydration to HMF. Also formic acid is used as source of hydrogen to transform HMF into 2,5-dihydroxymethylfurfural (DHMF) and finally acts as catalyst to DMFH deoxygenation to DMF.

3.1.1.2. Hydrogenation of furfural to 2-methyl furan (2-MF) or sylvan

Through the hydrogenation of furfural, furfuryl alcohol, methyl furan and 1,5-pentanediol can be obtained.¹⁰³⁻¹⁰⁴ Different Cu based catalysts such as Raney-Cu, Cu/alumina, and carbon supported Cu chromite were reported to be selective for 2-MF through furfuryl alcohol although catalyst deactivation was an important drawback. In order to overcome this problem, some authors have performed the hydrogenation of furfural under milder reaction conditions using palladium.¹⁰⁵ For example the hydrogenation of furfural in different solvents has been performed with H₂ (0.1 MPa) at 291 K using a polymer supported Pd complex achieving 100% yield of 2-MF after 1h.

3.1.1.3. Hydrogenation of furfural to 2-methyltetrahydrofuran (MTHF)

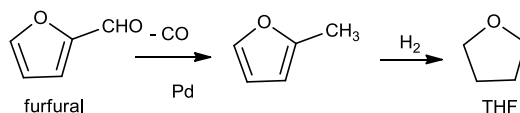
MTHF can be obtained by hydrogenation of gamma-valerolactone as was discussed above, and by hydrogenation of furfural in two pathways. In the first one 2-MF is produced followed by a ring hydrogenation. It has been proposed¹⁰⁶ that Ba/Mn-promoted Cu-chromite catalyst can produce 2-MF (0.1 MPa of H₂ at 175 °C) which is subsequently introduced in a second reactor where is hydrogenated to MTHF using Ni-based catalyst. Recently a two step catalytic process¹⁰⁷ to produce MTHF using Cu-chromite and Pd/C under supercritical CO₂ has been also proposed. An interesting feature of this process is that by adjusting the temperature of each reactor it is possible to obtain furfuryl alcohol, tetrahydrofurfuryl alcohol, 2-MF, MTHF or furan. Also, supported noble-metal catalysts under harsher hydrogenation conditions (20 bar) leads to a complete hydrogenation of the furanic ring to produce MTHF (Scheme 13).



Scheme 13. Pathways for the production of MTHF

3.1.1.4. Hydrogenation of furfural to tetrahydrofuran

Tetrahydrofuran (THF) can be obtained by decarbonylation of carbonyl group of furfural under reductive conditions using Pd based catalysts followed by hydrogenation of furan formed in the presence of a variety of metal catalyst.¹⁰⁸ (Scheme 14). THF can be blended with gasoline, however, due to its high volatility (boiling point = 339 K) and its carcinogenic activity it has low potential to be used as gasoline blending.

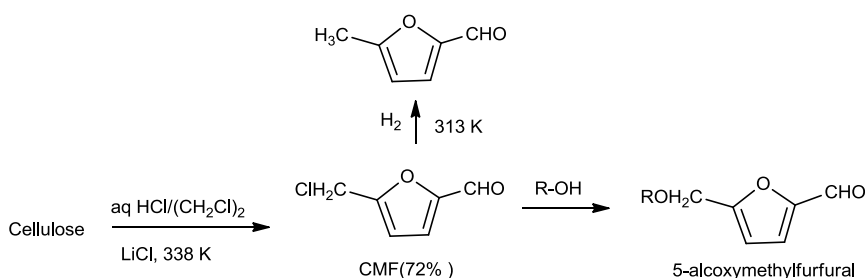


Scheme 14. Pathways for the production of THF

3.1.2. Etherification of HMF: Synthesis alkoxyethyl furfural derivatives

New bio-based chemicals called “*furanics*”, which are obtained by etherification of HMF with methanol or ethanol have been introduced as valuable components for a range of diesel or jet applications.¹⁰⁹ Thus, 5-(ethoxymethyl)furfural-2-carboxaldehyde (EMF) is a liquid with a high boiling point (508 K), recognized as an excellent additive for diesel that presents a reasonable energy density (8.7 kWh/L) compared with gasoline (8.8 kWh/L) and diesel (9.7 kWh/L). It was found that blend in commercial diesel in engine test, produces a significant reduction in soot (fine particulates) and in SO₂ emissions.¹¹⁰

5-Alcoxyethylfurfural ethers can be obtained from 5-chloromethylfurfural (CMF) following the Williamson reaction. The CMF can be directly obtained from cellulose (71% yield) using LiCl in concentrate hydrochloric acid.¹¹¹ CMF can be converted into biofuel candidates such as EMF and 5-MF by reacting with ethanol and by catalytic hydrogenation respectively. (see Scheme 14).



Scheme 15. Synthesis of 5-alcoxyethylfurfural from 5-(chloromethyl)furfural (CMF)

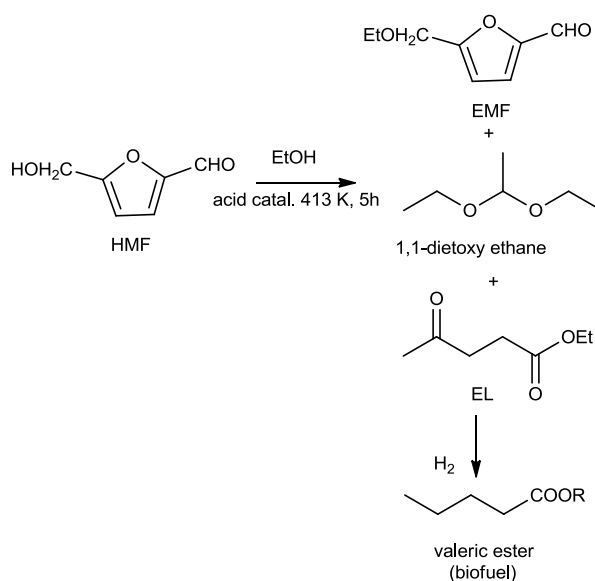
Although near quantitative yield of EMF can be obtained by the nucleophilic substitution of CMF with ethanol at room temperature,¹¹¹ however HCl is formed which is problematic from the point of view of its recycle and waste disposal problems. Moreover, the introduction of

unreacted halides into automobile fuel system can cause premature deterioration. Thus, for large scale synthesis of EMF, other alternative routes are preferred.

The most interesting routes to obtain EMF are: a) the direct etherification HMF with ethanol and b) starting from hexoses via a one pot strategy, which integrates dehydration to form HMF followed by etherification reaction.

Homogeneous and a variety of heterogeneous acid catalysts such as sulfonic acid resins,¹¹² organic-inorganic hybrid solid ($[\text{MIMBS}]_3\text{PW}_{12}\text{O}_{40}$),¹¹³ mesoporous materials¹¹⁴ and sulphated zirconia supported over mesoporous silica¹¹⁵, have been used to prepare EMF with variable success by reacting HMF with ethanol or others alcohols. Che et al.¹¹⁴ have prepared the high dispersed $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{MCM-41}$ nanospheres, as solid acid catalyst to obtain EMF starting from HMF. It was found 84% of selectivity to EMF when HMF conversion reaches 92% after 4h. The catalysts could be reused several times without lost of activity. Gruter¹¹⁶ describes the preparation of t-butoxymethylfurfural by reacting HMF and t-butanol (t-butanol/HMF molar ratio= 2) in the presence of Montmorillonite K10 and zeolite HY. Reactions performed at 373 K under 12.5 bar of nitrogen give HMF conversions between 49-59 % with selectivities to the ether between 76-79 %.

The etherification of HMF with ethanol has been reported¹¹⁵ using a series of mesoporous material (Al-MCM-41) with different Si/Al ratio, zirconia (ZrO_2) or sulphated zirconia supported over mesoporous silica (SBA-15), and the results were compared with an homogeneous acid catalyst such as sulfuric acid and a strong-acid heterogeneous resin-type Amberlysts-15 (see Table 4). Along with the desired ether 5-(ethoxymethyl)furfural (EMF) other intermediate valuable products such as 1,1-diethoxy ethane (acetal) and ethyl levulinate (EL) (Scheme 16) were also obtained in different yields, which formation is related to the presence of Bronsted and/or Lewis acidity on the catalyst.



Scheme 16. Different products obtained in the etherification of HMF with ethanol

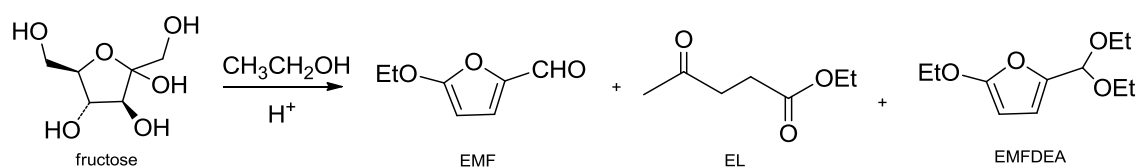
Interestingly, ethyl levulinate is an intermediate for the production of valeric ester biofuel additive, while the 1,1-diethoxyethane (acetal) is an additive for biodiesel which reduces the emission of CO₂ and also contribute to a marked decrease in particle number emission. As can be seen in Table 4, sulfuric acid, Amberlysts15 and Al-MCM-41(25) bearing strong Bronsted acidity favor the formation of EL, meanwhile catalysts with strong Lewis acidity such as ZrO₂-SBA-15 or Al-MCM-41(50) (which present extra framework Al⁺³ sites) perform a higher selectivity to the ether (EMF). When weaker acid catalysts such as Al-MCM-41(75) and pure SBA-15 are used in the etherification reaction the acetal is the main product observed. Thus, by tuning the acidity of the catalyst different biofuels such as valeric biofuels can be obtained. This process will be an alternative route for the that patented by Shell which consists in the preparation of gamma-valerolactone starting from levulinic acid, which is hydrogenate to valeric acid and then esterified to obtain valerate esters.⁶³

Table 4. Results of etherification of HMF with ethanol in the presence of acid catalysts

Catalyst	HMF conv.(%)	Yield (%) EMF	Yield (%) EL	Yield (%) acetal
SBA-15	75	-	-	54
Z-SBA-15	100	76	23	-
SZ-SBA-15	100	62	35	-
MCM-41(25)	100	37	47	12
MCM-41(50)	100	68	10	13
MCM-41(75)	61	-	-	19
Amberlyst-15	100	-	>99	-
H ₂ SO ₄	100	3	96	-

Reaction conditions: HMF (2.5 mmol), ethanol (3.4 mL), at 413 K, 2h

HMF ethers can also be obtained by reacting hexose-containing starting material with alcohols in the presence of homogeneous (hydrochloric acid)¹¹⁷ or heterogeneous catalysts such as zeolites, Montmorillonite and acidic resins.¹¹⁸ For instance, Lai et al.¹¹⁷ perform the transformation of fructose into hydroxymethylfurfural in hydrochloric acid using different alcohols as solvents (methanol, ethanol, isopropanol, and *tert*-butanol) at 393 K. Thus, when methanol and ethanol was used, a selectivity of 12 % and 37 % respectively to the corresponding HMF ethers have been reported. Starting from fructose and a mixture of alcohols (methanol, ethanol and n-butanol), 81.8 % conversion of fructose with selectivities to the corresponding ethers of 14.9 %, 14.9 % and 5.2 % were achieved in the presence of Beta zeolite working at 12.5 bar of nitrogen and 423 K.¹¹⁸ Balakrishnan et al.¹¹² have performed recently the etherification of HMF and its sugar precursor D-fructose with ethanol and butanol using sulfuric acid, and different acid resins such as Amberlyst, Dowex (Table 5). In all cases, a mixture of 5-(alcoxymethyl)furfural, 5-(alcoxymethyl)furfural dialkylacetal (EMFDEA) and alkyl levulinate (EL) were obtained (Scheme 17). The authors found that using sulphuric acid, lower temperatures favored the formation of 5-(alcoxymethyl)furfural and 5-(alcoxymethyl)furfural dialkylacetal meanwhile elevated temperatures favored alkyl levulinate selectively. The dehydrative etherification of fructose occurred at a slightly higher temperature than the etherification of HMF. Among the heterogeneous catalyst screened, Sulfonic acid functionalized resin Amberlysts-15 was found the most active for this reaction.



Scheme 17. One pot dehydration-etherification of D(-)-fructose in ethanol

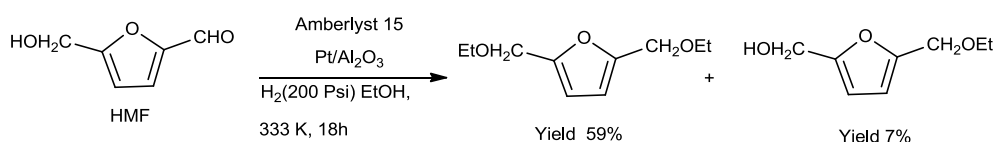
Table 5. Results of etherification of HMF and one pot dehydration etherification of fructose in ethanol as solvent

Starting material	Catalyst (Reaction conditions)	Yield(%)	Yield(%)	Yield(%)
		EMF	EL	EMFDEA
HMF	H ₂ SO ₄ (5 mol%, 348 K, 24h)	81.4	16	traces

HMF	H ₂ SO ₄ (5 mol%, 393 K, 30h)	-	58	-
Fructose	H ₂ SO ₄ (10 mol%, 373 K, 24h)	70	18	traces
Fructose	H ₂ SO ₄ (10 mol%, 393 K, 30h)	-	55	-
HMF	Amberlyst 15(5 mol%, 348 K, 24h)	55	8	31
HMF	DowexDR2030 (5 mol%, 348 K, 24h)	57	8	33
Fructose	Amberlyst 15(10mol%, 110 °C, 30h)	71	16	10
Fructose	DowexDR2030(10mol%, 110 °C, 30h)	68	16	6

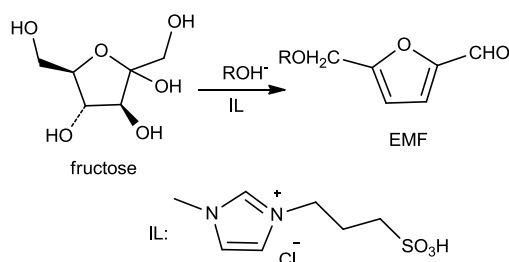
Starting material 1 mmol in 2 g of ethanol

Additionally, 2,5-bis(alcoxymethyl)furan (Scheme 18) was obtained in reasonable yields by one pot reductive etherification starting from HMF and one pot sequential dehydration/reductive etherification from D-fructose. It was found that alumina supported Pt and PtSn alloys were very active and selective catalysts for the reduction of carbonyl group of HMF yielding 50 % and 64 % of the target product respectively. 2,5-Bis(ethoxymethyl)furan is considered as potential biodiesel fuel due to its stability, low freezing points and high cetane number.



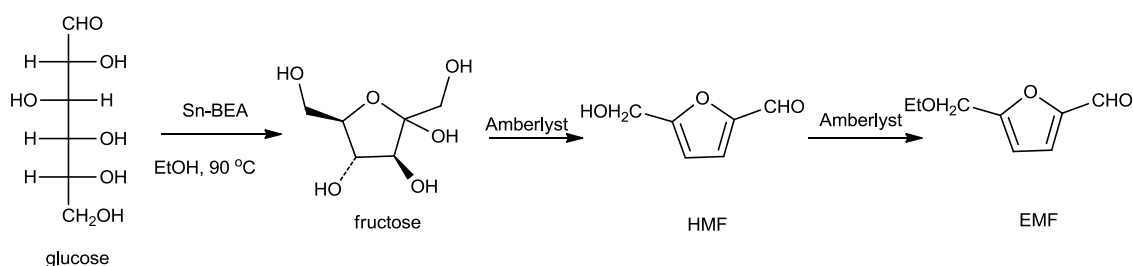
Scheme 18. One pot reductive etherification of HMF

Yang et al.¹¹⁹ reported the production of EMF from fructose in a yield of 65 % catalyzed by the Keggin-type heteropoly acid such as H₃PW₁₂O₄₀ under microwave heating. The synthesis of 5-alcoxymethylfurfural ethers directly from fructose and alcohols (methanol and ethanol) using sulfonic acid functionalized ionic liquids (imidazolium propanosulfonic acids) as catalysts in a biphasic system has been achieved.¹²⁰ For example, when fructose reacts with ethanol in hexane as co-solvent at 372 K, 54% yield of EMF and 6% of ethyl levulinate were obtained after 80 min (Scheme 19).



Scheme 19. Synthesis of EMF directly from fructose and alcohol in presence of an ionic liquid

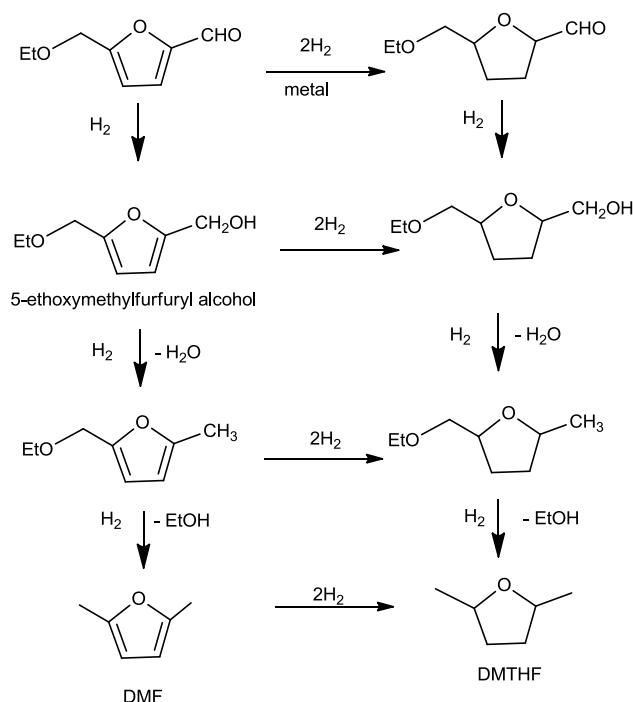
A one pot dehydrative etherification of fructose into EMF using a stable solid heteropolyacid-based ILs hybrid catalyst has been presented by Liu et al.¹¹³ Thus, using methylimidazolebutylsulfate phosphotungstate ($[\text{MIMBS}]_3\text{PW}_{12}\text{O}_{40}$) as catalyst, EMF was obtained in 90.5% yield in 24 h at 363 K. The catalyst was reused several times without loss of activity. The one pot synthesis of EMF starting from glucose has been reported using Sn-BEA zeolite and Amberlyst as catalysts in a single reactor at 363 K.¹²¹ The authors found that the acidic Lewis catalyst Sn-Beta zeolite, catalyzes the isomerization of glucose into fructose in ethanol, while Amberlyst 131 catalyzes selectively the dehydration of fructose into HMF and the subsequent formation of EMF. When both catalysts were combined in two-steps process, glucose could be converted to EMF in 31% yield (Scheme 20).



Scheme 20. One pot dehydrative etherification of glucose into EMF

Additionally, 5-Ethoxymethylfurfural can be hydrogenated to obtain 5-ethoxymethylfurfuryl alcohol which has been proposed as a potential additive for diesel fuel. The selective hydrogenation of 5-ethoxymethylfurfural has been performed over alumina-supported bimetallic catalysts.¹²² The bimetallic catalysts are composed of one

majority metal component such as Au, Cu, Ir, Ni, Pd, Pt, Rh, and Ru and one promoter metal (Bi, Cr, Fe, Na, Sn, W). In all cases 5-ethoxymethylfurfuryl alcohol was the main product obtained, together with some by products that include dimethyltetrahydrofuran generated by ring hydrogenation and some oligomers (Scheme 21). It was found that Ir/Cr supported on gamma-alumina is the most promising metal, yielding 99% of 5-ethoxymethylfurfuryl alcohol when using 1,4-dioxane as a solvent at 353 K. However, when diethyl carbonate was used as a solvent only 2,5-diethoxymethylfuran was obtained. When using an excess of hydrogen at 393 K in the presence of catalysts containing Cu or Ni, an over hydrogenation occurs giving as main product of 2,5-dimethyltetrahydrofuran (DMTHF) (40% selectivity) while at higher temperatures dimethylfuran and dimethyl tetrahydrofuran were obtained (Scheme). Lower activity was found for metal supported on silica catalysts.¹²³ Pt and Rh supported on silica were the most efficient and selective catalyst to obtain 5-ethoxymethylfurfuryl alcohol. For instance, 100% selectivity to 5-ethoxymethylfurfuryl alcohol was found for conversions up to 66%.

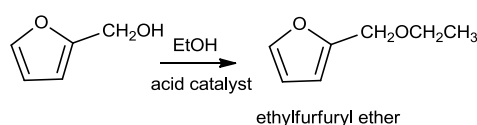


Scheme 21. Pathways in the hydrogenation of ethoxymethylfurfural

3.1.3. Etherification of furfuryl alcohol: Synthesis of Ethylfurfuryl ether (EFE)

Ethylfurfuryl ether (EFE) has been proposed as gasoline component due to its physical properties. It can be obtained by etherification of furfuryl alcohol with ethanol in the

presence of acid catalysts (Scheme 22). Thus, when the reaction was performed at 423 K in diluted sulfuric acid the EFE selectivity was approximately of 30 % at 20-90 % conversion. The formation of EFE was accompanied by heavy byproducts at approximately 20% conversion. Heterogeneous catalyst such as ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3=30$) have also been reported for this etherification and a maximum yield of 50 % at 80% conversion was reached working at 398 K.¹²⁴ However, lower yields of EFE were obtained using ZSM-12, ZSM-35, HBeta, HY, HMordenite and HFerrierite zeolites.



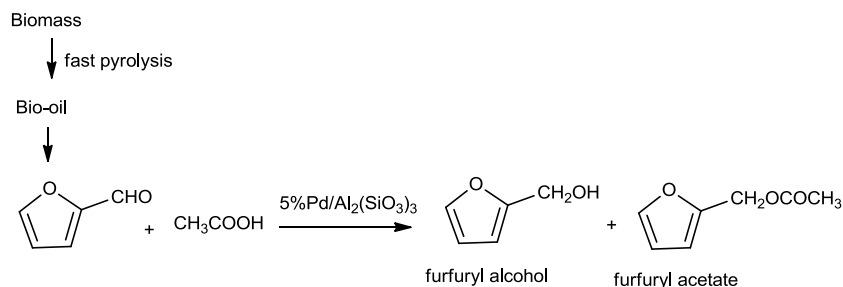
Scheme 22. Synthesis of ethylfurfuryl ether from furfuryl alcohol

3.1.4. Esterification of HMF and furfuryl alcohol with acetic acid: Synthesis of furan acetate esters

The production of HMF and furfuryl alcohol esters by transesterification or esterification is another approach to afford new furan derivatives that can be used as a fuel blending agents. Particularly, acylated product (5-acetyl-HMF) has higher energy density (8.7 kWh/L) compared with ethanol and similar to that of gasoline (8.8 kWh/L). Biocatalyst (lipases)¹²⁵ as well as different homogeneous and heterogeneous catalysts such as sulphuric acid, metal chloride, transition metals have been used with good success to perform the esterification of HMF with acetic acid or anhydride.^{102, 126} For example Gruter et al.¹²⁶ have patented the manufacture of HMF ester by reacting hexose containing starting material or HMF with an alcohol or an organic acid dissolved into an ionic liquid in the presence of metal chloride as catalyst.

It is known that many problems limit bio-oil application, among them the corrosiveness due to the organic acids (which results in pH=2-3) and the instability due to the considerable amounts of aldehydes (i.e. furfural) which can suffer polymerization and condensation reactions. To overcome this problems different approaches like hydrodeoxygenation¹²⁷ esterification¹²⁸ have been reported for the transformation of corrosive nonflammable acids and reactive unstable aldehydes in more stable combustible esters and alcohols. Yu et al.¹²⁹ have presented a one step hydrogenation-esterification of furfural with acetic acid, the main components of crude bio-oil, over

bifunctional catalyst (Scheme 23) as a promising method for efficient upgrading of bio-oil.



Scheme 23. Hydrogenation-esterification of furfural and acetic acid over bifunctional catalyst.

We have summarized in Table 6 some of the results of hydrogenation-esterification on different bifunctional catalyst. In all cases, the desired products, furfuryl alcohol (FOH) and furfuryl acetate (FACE) were obtained. It was shown that 5%Pd/Al₂(SiO₃)₃ composite catalyst present best selectivity (66.4 % to furfuryl alcohol and ester (52.8% and 13.6% respectively). The authors claim that the better performance over 5%Pd/Al₂(SiO₃)₃ composite bifunctional catalysts can be attributed to its better cooperative effect between metal and acid sites. 2-Methylfuran (2-MF) was also formed from the over hydrogenation product of furfural.

Table 6 .One step hydrogenation-esterification of furfural with acetic acid over bifunctional catalysts

Catalyst	Conv. (%)	Selec. (%)	Selec. (%)	Selec. (%)	Selec. (%)
	Furfural	FOH	FACE	2-MF	By-Prod.
5%Pd/C +Al ₂ (SiO ₃) ₃	69.4	19.7	9.1	25.8	45.4
5%Pd/C	41.2	35.0	0	21.6	43.4
Al ₂ (SiO ₃) ₃	18.6	0	0	0	100

5%Pd/Al ₂ (SiO ₃) ₃	56.9	57.2	13.6	0	33.6
5%Pt/Al ₂ (SiO ₃) ₂	50.2	53.2	13.5	0	34.7
5%Cu/Al ₂ (SiO ₃) ₂	26.1	29.9	6.1	0	64.0
5%NiAl ₂ (SiO ₃) ₂	23.9	25.9	5.0	0	69.0

Reaction conditions: furfural: 0.10 mmol, acetic acid 0.10 mmol in 10 ml Toluene, P_{H2}= 2 MPa, 423 K, 4h , 0.4g catalyst. In composite 5%Pd/C(0.4g) +Al₂(SiO₃)₃(0.4g)

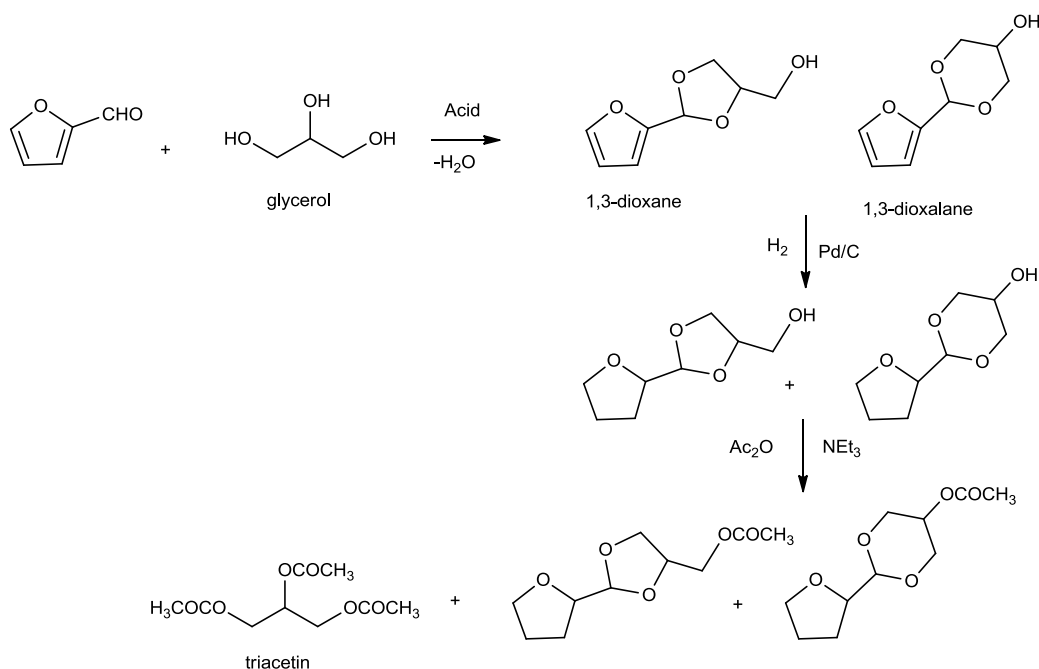
3.1.5. Acetalization of furfural and HMF with glycerol: Synthesis of glyceril acetals of furfural derivatives

Acetalization of furfural and its derivatives with glycerol gives a mixture of cis and trans isomers of five- and six- membered furans named 1,3-dioxolane and 1,3-dioxane respectively. They have been described as additive of biodiesel fuel¹³⁰ since they can improve the viscosity and cold properties of biodiesel, and have reasonable oxidation stability and flash point.¹³¹ Acetalization of 5-HMF with glycerol has been performed with p-Tolunesulfonic acid in benzene as solvent, giving the corresponding 2-(2-furyl)5-hydroxy-1,3-dioxane and 2-(2-furyl)4-hydroxymethyl-1,3-dioxalane in 70-75% yields after 3-3.5 h.¹³²

Recently, Mallesham et al.¹³³ have designed efficient Mo and W-promoted SnO₂ solid acids for acetalization of glycerol with furfural and its derivatives under solvent free at room temperature. The authors found that the addition of Mo⁺⁶ ions to SnO₂ increase its activity due to the presence of higher amounts of acidic sites, large BET surface area, lattice defects and redox properties. Thus, 51, 67 and 75% of glycerol conversions were obtained with SnO₂, WO₃/SnO₂ and MO₃/SnO₂ catalysts respectively.

A new strategy to obtain additives for biodiesel consists in the hydrogenation of cyclic acetals derived from furfural and glycerol, followed by acetylation process (Scheme 24).¹³⁴ For instance, acetalization of furfural with glycerol was carried out in the

presence of homogeneous and heterogeneous catalysts with a stream of dry nitrogen at 373 K. Among the homogeneous Lewis acid studied (ZnCl_2 , AlCl_3 , $\text{Cu}(\text{OTf})_2$, NiCl_2 , $\text{Ag}(\text{OTf})$, AgBF_4), ZnCl_2 resulted the most active catalyst (90% yield after 2h). Similar results were given using aluminosilicate MCM-41 and Montmorillonite K10 as catalyst (yield 80%). The furan ring of acetals were hydrogenated subsequently under mild conditions (2.76 MPa, H_2) using Pd/C yielding a mixture tetrahydrofuryl-1,3-dioxacyclanes. Then, the hydroxyl group was reacted with acetic anhydride yielding a mixture of tetrahydrofuryl-1,3-dioxacyclanes acetates and triacetin (molar ratio 4:1), and the viability of hydrogenated and acetylated mixture as biodiesel additives was studied.



Scheme 24. Additives for biodiesel from acetalization of furfural with glycerol

3.2. Furan derivatives as platform molecules for liquid hydrocarbon fuels

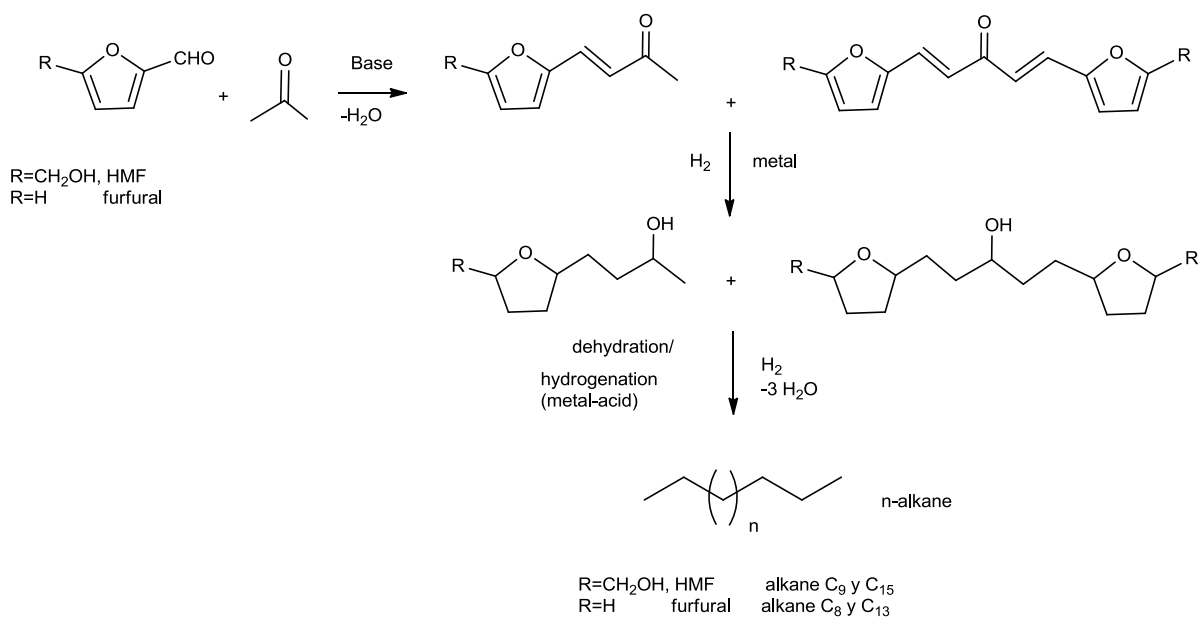
Furan platform molecules only contains C₅ and C₆ carbons since they are formed from hexoses and pentoses. Therefore, in order to upgrade these molecules into liquid alkanes with higher number of carbons able to be used in gasoline, diesel and jet engines different strategies for C-C coupling have been proposed based on the reactivity of the carbonyl group and the furan aromatic ring. These approaches are namely aldol

condensation and hydroxyalkylation/alkylation of the furan derivatives which we will discuss in this section.

3.2.1. Aldol condensation

Aldol condensation is a C-C bond formation reactions that occurs between two carbonyl compounds with a reactive α -hydrogen on at least one of the carbonyls, and which is catalyzed by acids or bases. Recently it has been used as a strategy to obtain hydrocarbons in the diesel fuel range starting from biomass derived compounds. Evidently and additional hydrogenation or a deep dehydrodeoxygenation step are required in order to transform the large oxygenate molecules formed (aldol or α,β -unsaturated carbonyl compounds) into a mixture of alkanes for high quality diesel.

Several authors reported the aldol condensation reactions of HMF and other furfural products with carbonyl compounds, mainly acetone (which can be also obtained by fermentation of biomass) as a synthetic strategy for the synthesis of pharmacological compounds and useful intermediates for the synthesis of biofuels¹³⁵⁻¹³⁷ (Scheme 25).



Scheme 25. Coupling of furfural or HMF with acetone and subsequent dehydroxygenation to alkanes

Aldol condensation between furan derivatives has been carried out with homogeneous catalysts such as aqueous NaOH solutions,¹³⁸⁻¹³⁹ and zinc and Ytterbium salts of proline.¹⁴⁰ Among the heterogeneous basic catalysts, dried chitosan-gels¹⁴¹ mixed oxides,¹⁴²⁻¹⁴⁴ layered double hydroxides,¹⁴⁵ and sodium and nitrogen substituted zeolites¹⁴⁶ have been used with different success. In all cases not only a single condensation adduct is obtained but it is possible a second condensation between the former and other HMF or furfural giving a bis-adduct molecule with higher carbon atoms (Scheme 24). For instance, the aldol condensation of various furfurals (furfural, HMF and methyl furfural) and ketones such as acetone, dihydroxyacetone, acetol, 2-hexanone and 3-hexanone derived from biomass, give single and double condensation products in a biphasic system using NaOH as catalysts.¹³⁸ The system employs an aqueous phase with NaOH catalyst and an organic extracting phase to remove the aldol products from homogeneous catalyst. The final distribution and yield of products can be controlled by adjusting the molar ratio of the ketone to furfural derivative and by changing the amount of NaOH. In the case of the condensation of furfural with acetone high yields of single and double condensation products can be achieved. However, when HMF was used, the presence of acidic by-products coming from the degradation of HMF that neutralize the base, limits the formation of condensation products.

Mixed oxides with different basic strength (MgO-ZrO₂, MgO-Al₂O₃ and CaO-ZrO₂) have been also used for aldol condensation of furfural with acetone in aqueous media.¹⁴⁴ In all cases a mixture of 4-(2-furyl)-3-buten-2-one (C₈) and 1,5-bis-(2-furanyl)-1,4-pentadien-3-one (C₁₃) were obtained, and the order of activity was related with the concentration of medium strength basic sites i.e. Mg-Zr > Mg-Al > Ca-Zr. Thus, when the aldol reaction was performed in the presence of Mg-Zr mixed oxide in a molar ratio furfural/acetone 1:1, at 325 K 63% yield of C₁₃ was obtained, whereas 43 and 15.5 % were found for Mg-Al and Ca-Zr respectively. The catalytic performance of the Mg-Zr mixed oxide can be considerably increased by supporting the mixed oxide on mesoporous carbons, achieving 96 % conversion of furfural with 88 % selectivity for C₁₃ and C₈ adducts. The improved performance is attributed to a more appropriated basic site distribution and by higher interaction of the reactants with the carbon surface.¹⁴⁷ Also, layered double hydroxides (Mg-Al-LDH) prepared by hydration of the corresponding mixed oxide have been tested in aldol condensation of furfural with acetone at 100 °C. The highest furfural conversion (78.6 %) and selectivity to 4-(2-

furyl)-3-buten-2-one (C₈) of 72.3 % was obtained using a Mg-Al-LDH with Mg/Al molar ratio of 2.5.¹⁴⁸

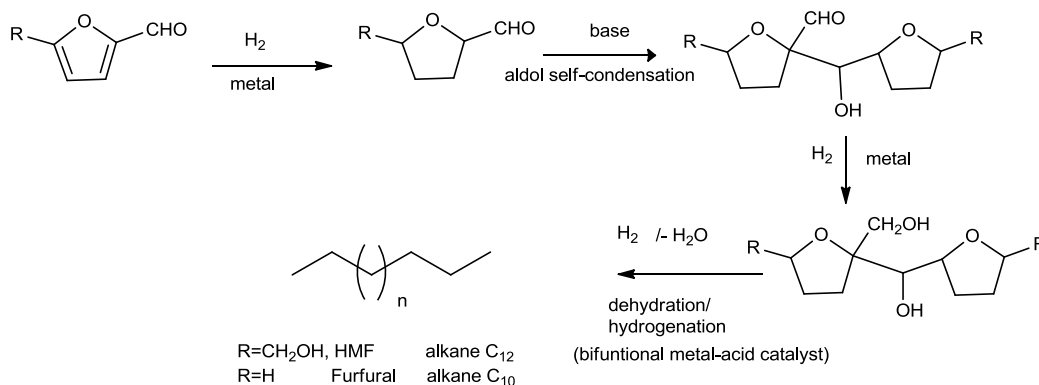
Shen et al.¹⁴⁶ performed the aldol condensation between HMF and acetone or propanal in the presence of different base catalysts such as MgO-ZrO₂, NaY zeolite and nitrogen substituted NaY at 120 °C. The authors found that in the condensation with acetone a mixture of the mono and bis-adduct was obtained, while with propanal 100% yield of double aldol condensation was produced.

Dumesic et al.^{142-143, 149} have proposed a process for obtaining diesel fuels of high quality from condensation of HMF or furfural with acetone involving the aldol condensation, followed by hydrogenation and deep dehydrodeoxygenation. Condensation of HMF with acetone was carried out in a biphasic reactor where the furan compound dissolved in THF is contacted with aqueous NaOH solution at room temperature. This protocol allows the continuous extraction of aldol compounds into the organic solvent. The single condensation product (4-(5-(hydroxymethyl)furan-2-yl)but-3-en-2-one), a C₉ intermediate, can additionally react with a second molecule of HMF to produce a C₁₅ oxygenated fuel precursor (Scheme 25). Finally, the hydrogenated aldol compounds are subjected to a hydrogenation/dehydration/ring opening process in the presence of bifunctional catalysts such as, Pd/Al₂O₃ (at 373-413 K and 25-52 bar of H₂) and Pt/NbPO₅ (at 528-568 K and 60 bar of H₂), producing after ring opening a mixture of linear C₉ and C₁₅ alkanes in 73 % yield.

Recently Chatterjee et al.¹⁵⁰ described the synthesis of liquid linear alkanes by hydrogenation and dehydration/hydrogenation of 4-(5-(hydroxymethyl)furan-2-yl)but-3-en-2-one. The process consists in i) the aldol condensation of HMF and acetone using NaOH as catalyst, ii) hydrogenation and ring opening by dehydration/hydrogenation in supercritical carbon dioxide (scCO₂), at 353 K, P_{CO₂}= 14 MPa, P_{H₂}= 4 MPa in the presence of Pd/Al-MCM-41 catalyst. The process yields C₉ linear alkanes with >99% selectivity.

Pd supported on differed mixed oxides has been utilized as bifunctional basic-metal catalyst for coupling aqueous phase aldol condensation of furfural and HMF with acetone followed by hydrogenation.^{143, 151} For instance, with Pd/MgO-ZrO₂ yields higher than 80% for the aldol condensation adducts were obtained when working at 53-353 K.¹⁴³ On the other hand, the selective hydrogenation of the aromatic ring of HMF

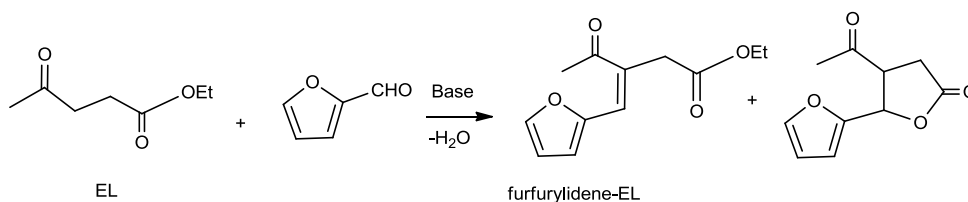
and furfural give 5-hydroxymethyltetrahydrofurfural and tetrahydrofurfural which after self condensation followed by hydrogenation/dehydration process produce C_{12} or C_{10} alkanes respectively (Scheme 26).¹⁵²



Scheme 26. Coupling furfural or HMF and subsequent hydrodeoxygenation to alkane

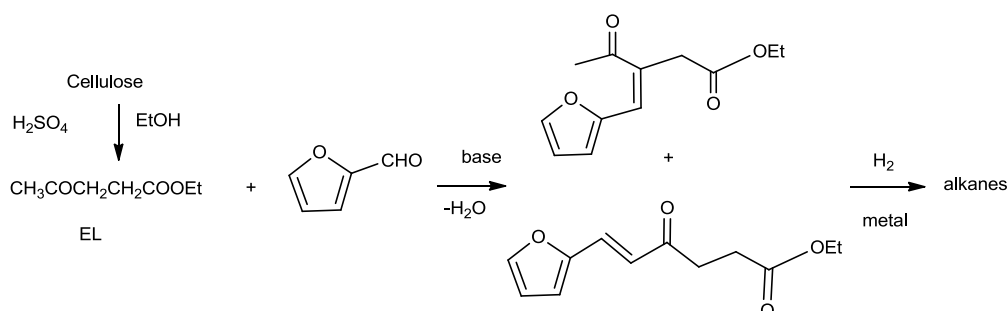
One disadvantage for the production of C_9 alkanes, in the range of jet and diesel fuels, from the aldol condensation of HMF with acetone is the high consumption of hydrogen, 8 mol of hydrogen per mol of alkane.¹⁴² However, this process allows for selective production of linear alkanes with minimal carbon branching, which is not possible with hydrogen-neutral processes such as alkene oligomerizations.

Levulinic acid or its ethyl ester (EL) can also be condensed with furfural to give a coupling product which after hydrodeoxygenation can be used as a diesel component (Scheme 27). For instance, solid base catalyst such as Cs/MgO, MgO, Sn/Al₂O₃, La/Al₂O₃, K/ZnCrO_x, have been used for the aldol condensation of EL with furfural at 443-503 K (EL/Furfural molar ratio =1) under reactive distillation of water. In all cases a mixture of the desired product furfurylidene-EL and its corresponding branched isomer were formed with a maximum yield of 20-25% which were converted subsequently into higher oligomers in approximately 80% yield. It was found that the catalytic activity of the more basic Mg and La oxides was lower than of Sn and Zn oxides.⁹¹



Scheme 27. Aldol condensation of furfural with ethyl levulinate (EL).

Recently a process to produce fuel components and chemicals starting from cellulose has been patented.¹⁵³ The process consists in the preparation of levulinic acid and levulinic acid esters by thermocatalytic reaction of cellulose, which were subsequently condensed with aldehydes (e.g. furfural), ketones, esters, ketoacids, in acidic or basic media (PTSA, Amberlyst-15, NaOH, Hydrotalcites, MgO, etc.). The condensation product, is hydrogenated and/or dehydrodeoxygenated using a variety of metals such as Pd, Pt, Ru, Fe, Ni supported on carbon or alumina giving good conversions to alkane mostly in the range of C₉-C₁₅ (Scheme 28).

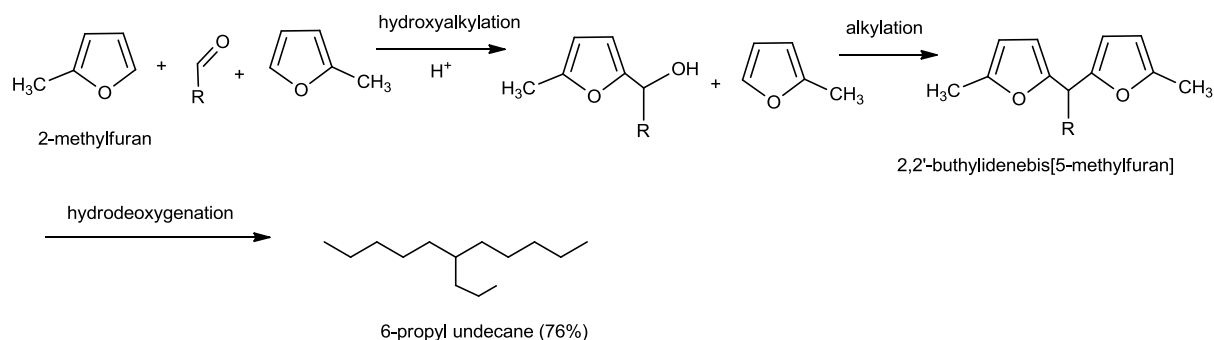


Scheme 28. Aldol condensation of furfural with ethyl levulinate and hydrogenation to alkanes.

3.2.2. Hydroxyalkylation/alkylation of 2-methylfuran

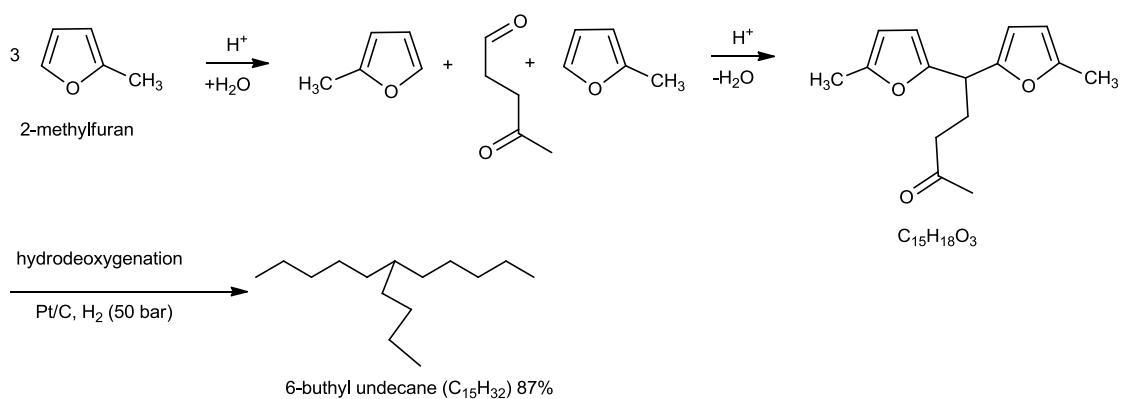
Recently Corma et al.¹⁵⁴⁻¹⁵⁶ have designed a sustainable process named “Sylvan process” for producing long chain alkanes with excellent cetane number and pour point. The process involves two consecutive catalytic steps, a hydroxyalkylation/alkylation of three molecules of 2-methylfuran (sylvan) or hydroxylation of sylvan with aldehydes or ketones to form an oxygenated hydrophobic diesel precursor with an adequate number

of carbon atoms. In a second step, a complete hydrogenation to a mixture of alkanes with excellent properties as diesel fuel is achieved (Scheme 29).



Scheme 29. Hydroxyalkylation/alkylation of 2-methylfuran (Sylvan) with carbonyl compounds and deoxygenation to alkanes

For example, when the reaction of 2-MF and 1-butanal were carried in the presence of acid catalysts such as p-toluenesulphonic acid (PTSA) or Amberlyst-15 in absence of organic solvents at 333 K, 2,2'-buthylidenebis[5-methylfuran] diesel precursor was achieved in high yields. The second step, the hydrodeoxygenation of the 1,1-bissylvlalkanes (difuran) was performed in a fixed bed continuous reactor at 623 K passing hydrogen (50 bar). Complete hydrogenation of all unsaturated bonds in difuran and hydrogenolysis of all carbon-oxygen occur. Also, excision of the carbon-carbon bond adjacent to tertiary carbon atom in the middle of the undecane chain occurs at low levels, removing consequently a C₅ moiety. Among the different metallic catalysts tested for the hydrogenation step, good results were obtained when using platinum on carbon and alumina as catalysts. Thus, starting from 2-MF and butanal at the end of the process, 95% of the liquid organic products are alkanes with 76%, 17% and 2% of 6-propylundecane (C₁₄), n-nonane (C₉) and 4-propylnonane (C₁₂) respectively. The authors claim that the process is very stable at laboratory levels (more than 140 h) and produce diesel range products with excellent pour point (183 K) and cetane number (70.9) that are suitable for direct blending with conventional fossil diesel.(see characteristics of the resultant product in Table 7



Scheme 30. Hydroxyalkylation/alkylation of 2-methylfuran (Sylvan) and hydrodeoxygenation to alkanes

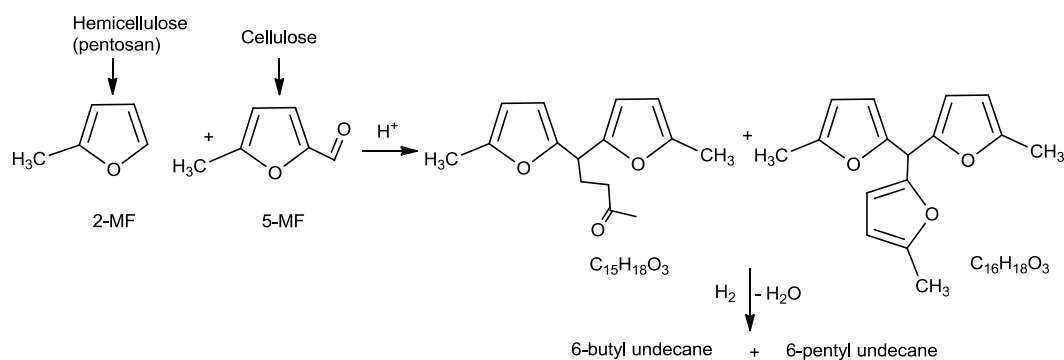
More importantly, when the reaction was performed with three molecules of 2-methylfuran in absence of another reactant and using sulfuric acid as catalyst the one step trimerization of 2-methylfuran takes place (Scheme 29). The trimerization of sylvan is a hydroxyalkylation/alkylation process that occurs between 2-methylfuran and a molecule of 4-oxopentanal which in turn is produced in situ by the acid catalyzed ring opening of a molecule of sylvan (see Scheme 30). High yield of difuran (77%) was achieved when using 24 wt % sulfuric acid in water after 16h at 333 K. Furthermore, the aqueous phase containing the sulphuric acid catalyst, can be separated from the organic compounds by simple phase separation and the acid catalyst can be reused several times. Hydrodeoxygenation of the C_{15} molecules diesel precursor was carried out in the presence of Pt/C (50 bar) and 633 K with very good performance. An excellent overall yield (87 %) of diesel starting from sylvan was achieved. The mixture can be blended directly with commercial diesel due to present adequate physical properties as can be seen in Table 7.

Table 7. Diesel properties of mixtures obtained from Silvan process

	Diesel A	Diesel B	Standard	Specification
Sulfur	<1	<1	ASTM D-2622	<10 ppm
Nitrogen	<1	<1	ASTM D-4629	-
Cetane number	70.9	72.2	ASTM D-613/8	Min 51
Upper pour point (°C)	-90	-75	ASTM D-97	
Cloud point (°C)	<-91	-80.6	ASTM D-2500	
Cold filter plugging point (°C)	<-51	-48	UNE-EN 116-98	Winter<-10

Diesel A obtained from the distilled precursor 1,1-bissilylbutane according to the process depicted in Scheme 29. Diesel B obtained from the precursor 5,5-bissilyl-2-pentanone according to the process depicted in Scheme 30.

The process is very general as observed from the hydroxyalkylation and alkylation of 2-methylfuran with different aldehydes (ethanal, propanal, pentanal, HMF and 5-methylfurfural), or ketones (2-pentanone and acetone) and α,β -unsaturated carbonyl compounds (4-methylpent-4-en-2-one) in acidic media (sulphuric acid or PTSA). In all cases, the corresponding 1,1-bissilylalkanes were obtained in good yields, being all compounds converted into premium diesel by deoxygenation process. For instance, the hydroalkylation/alkylation of sylvan with 5-methylfurfural in the presence of PTSA, gives a mixture of 93 % yield of 2,2',2''methylidenetris(5-methylfuran) and 2% yield of 5,5-bissilyl-2-pentanone, C₁₆ and C₁₅ oxygenated products which are precursor of diesel. After hydrodeoxygenation reaction in the presence of platinum on active carbon up to 89% of a mixture of 6-pentylundecane and 6-buthylundecane was obtained, giving an excellent quality diesel (Scheme 31).



Scheme 31. Hydroxyalkylation/alkylation of 2-methylfuran with 5-methylfurfural and hydrodeoxygenation to alkanes

Additionally, heterogeneous acid catalysts such as microporous and layered zeolites (Beta, USY and ITQ-2), a mesoporous material (MCM-41) and a sulfonic acid resins (Amberlyst 15 and Dowex 50) were tested for the hydroxyalkylation/alkylation reactions of 2-MF with butanal under solvent free conditions. It was found that delaminated ITQ-2 zeolite gives the best result due to its better accessibility to the acid sites (see Table 8).

Table 8. Results of hydroalkylation/alkylation of 2-MF with 1-butanal to give 2,2'-butylidenebis[5-methylfuran] in presence of different acid catalysts.

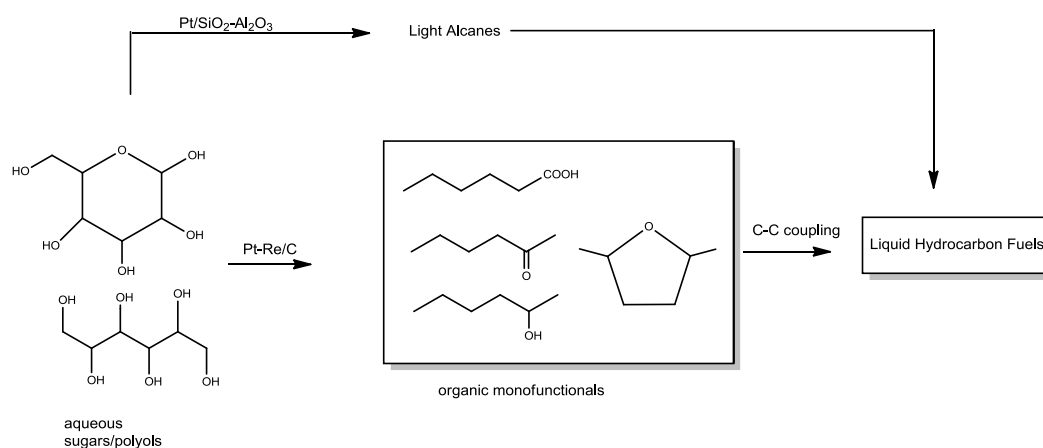
Catalyst	Si/Al ratio	r^o (mmolg ⁻¹ h ⁻¹)	Yield (%)
USY	20	331	53
Beta _{commercial}	13	101	67
Beta _{nanocrystalline}	15	111	59
Beta(OH)	13	72	34
Beta(F)	13	29	16
MCM-41	15	175	45
MCM-41	28	92	60
ITQ-2	32	382	86
Amberlyst 15 ^a		317	90
Dowex 50WX2-100 ^b		120	80

Reaction conditions: sylvan/butanal molar ratio 2:1, 50 mg catalysts, 323 K, 8h. ^a Concentration of active sites 4.7 meq/g. ^bConcentration of active sites 4.8 meq/g;. r^o : initial activity in mmol of product per g of catalyst per h; measured after 30 min reaction time.

4. Polyols as platform for liquid hydrocarbon fuels

Aqueous phase reforming (APR) of alcohols and polyols (methanol, glycerol, ethylene glycol, glucose, sorbitol) using platinum based catalysts, first introduced by Dumesic and co-workers,¹⁵⁷ is an interesting approach for the production of renewable hydrogen which can be used directly as energy, in hydrogen fuel cells or as external source of hydrogen for biomass upgrading processes. However, through the adequate selection of metal, support and reaction conditions, the selectivity of APR process can be tuned towards the production of light alkanes.¹⁵⁸ For instance, the aqueous phase reforming of methanol and ethylene glycol over Pt-black, and Pt supported on TiO₂, Al₂O₃ and ZrO₂ favors the C-C bonds cleavage producing selectively hydrogen,¹⁵⁹ while other metals such as Rh, Ru, and Ni favors the C-O cleavage, rather than C-C, leading to the production of alkanes.¹⁵⁸ The acidity of the reaction system has also influence on the selectivity towards alkanes, thus when solid acids such as SiO₂ or Al₂O₃, are used as supports or mineral acids such as HCl are added to the feed, the rates of dehydration and hydrogenation process increases compared with the rate of hydrogenolysis and reforming reactions leading to increased selectivity to alkanes. In fact, another strategy for the removal of oxygenated groups of polyols such as sorbitol, is through dehydration of hydroxyl groups followed by hydrogenation of the resulting unsaturated compounds. The process denoted as aqueous-phase dehydration-hydrogenation (APDH) can be performed over bifunctional catalysts bearing acidic and metal sites such as Pt/SiO₂-Al₂O₃¹⁶⁰ or Pt supported on niobium based solid acids¹⁶¹ at 520 K and near 50 bar. Dehydration of the hydroxyl groups takes place on the acid sites producing unsaturated species such as alkenes or carbonyl compounds and even heterocyclic ring structures, which are subsequently hydrogenated to alkanes. However, this strategy is limited to the production of alkanes with the same number of carbon atoms of the starting feedstock. An alternative approach which allows obtaining higher alkanes was developed by Kunkes et al.¹⁶² which consists of a two-step cascade process that combines oxygen removal and C-C coupling reactions (Scheme 32). Firstly, sugars and polyols are partially deoxygenated (up to 80 %) by C-O hydrogenolysis over a Pt-Re(10 wt%)/C catalyst at around 573 K. A mixture of different monofunctional organic compounds in the C₄-C₆ range which contains acids, alcohols, ketones and heterocycles and that separated spontaneously from the aqueous phase is obtained. An important point is that the hydrogen required for the deoxygenation is internally supplied by aqueous phase

reforming of a part of the feed on the multifunctional Pt-Re/C catalyst. In a subsequent step, this mixture of monofunctional compounds is upgraded to higher hydrocarbons through different C-C coupling reactions such as aldol and ketonization processes. However, a limitation of the process is the high cost of the catalyst.



Scheme 32. Routes for upgrading polyols to alkanes

5. Fuel additives and liquid hydrocarbons fuels from vegetable oils and fats

Triglyceride based biomass (such as vegetable oils, animal fats) can be directly converted into transportation fuels through three main processes: a) Transesterification of the triglyceride with lower alcohols (methanol and ethanol) giving biodiesel. b) catalytic cracking processes and c) hydrotreatment processes. Biodiesel is composed by fatty acid methyl or ethyl esters which can be directly blended with conventional diesel fuels, while products coming from catalytic cracking contain linear and cyclic paraffins, olefins, aldehydes, ketones and carboxylic acids. On the other hand, hydrotreatment of vegetable oils produce mainly a mixture of n-alkanes mostly in the range $\text{C}_{15}\text{-C}_{18}$ which are suitable as an alternative diesel fuel. Catalytic production of biodiesel¹⁶³⁻¹⁶⁹ and hydrocarbon biofuels through cracking and hydrotreating¹⁶⁹⁻¹⁷³ of triglycerides as well as fuel properties, advantages and drawbacks have been extensively studied and reviewed in literature and are out of the scope of this work. Therefore, in this section we will only discuss the main processes to produce fuel additives and hydrocarbon biofuels from triglyceride platform molecules, i.e. glycerol and fatty acids.

5.1. Fuel additives from glycerol

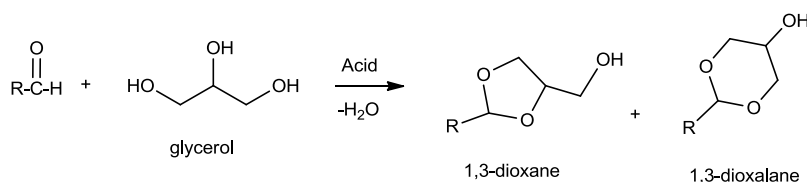
In the last years the increasing production of biodiesel has generated an important increase in the glycerol stock since stoichiometrically glycerol is produced by 10 wt% of total biodiesel production. This scenario has prompted an important research to find new applications for this low-cost platform molecule by converting glycerol to commodity chemicals through different routes such as reduction, oxidation, dehydration, etherification, esterification, oligomerization, acetalization and others¹⁷⁴. In fact, the synthesis of industrially useful chemicals from glycerol derived from biodiesel will be a key factor to increase the success of biodiesel production. Due to glycerol cannot be added directly to fuels since at high temperature glycerol is prone to decomposition and polymerization which lead to engine problems, another alternative is to convert glycerol into oxygenated compounds that can be used as fuel additives compatible with gasoline, and diesel. It has been reported that glycerol based additives are able to enhance cold flow and viscosity properties of liquid fuels, decrease the fuel cloud point, be used as antiknock additive for gasoline, improve octane rating, reduce greenhouse gas emissions and could replace the conventional and problematic methyl tertbutyl ether (MTBE).¹⁷⁵

The transformation of glycerol into oxygenated additives for fuels follows three main routes: acetalization with simple carbonyl compounds, etherification with olefins or lower alcohols (including glycerol oligomerization) and acetylation processes that we will discuss in this section.

5.1.1. Glycerol acetals

Acetalization of carbonyl compounds with alcohols is an acid catalyzed reaction which can be performed generally using homogeneous (usually HCl, H₃PO₄, p-toluenesulfonic acid) or a variety of heterogeneous acid catalysts such as zeolites¹⁷⁶⁻¹⁷⁷, supported metal oxides¹⁷⁸ or cationic resins¹⁷⁹, at moderated temperatures and in presence or absence of solvents.

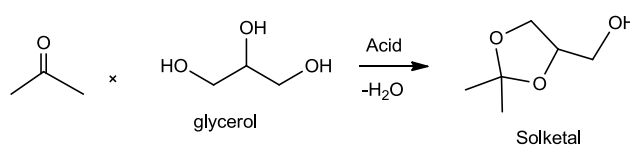
Particularly, glycerol reacts with simple carbonyl compounds giving isomeric six ((Z+E) 1,3-dioxan) and five-membered ((Z+E)-1,3-dioxolan) cyclic compounds (Scheme 33) which proportion depends on the catalyst, structure of the carbonyl compound and reaction parameters such as temperature and molar ratio of reactants.



Scheme 33. Acetalization of carbonyl compounds with glycerol

A variety of acetals of glycerol have been recognized as diesel fuel additives that reduce the emission of CO and hydrocarbons and when added to biodiesel they acts as cold flow improvers.¹³¹

The ketalisation of glycerol with acetone mainly yield 2,2-dimethyl-1,3-dioxolane-4-methanol, also known as solketal (Scheme 34) that constitutes an excellent compound for the formulation of gasoline, diesel and biodiesel fuels. For instance, Motta et al.¹⁸⁰ showed that solketal blended in 1, 3 and 5 vol% with regular gasoline reduced the gum formation and increased the octane number up to 2.5 points.



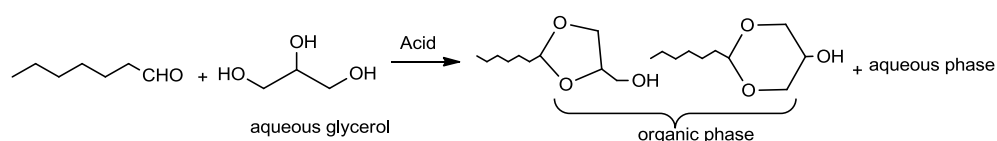
Scheme 34. Synthesis of solketal

Solketal has been prepared using conventional mineral acids,¹⁸¹ and different homogeneous catalysts such as Ir complexes¹⁸² or metal triflates.¹⁸³ Also a variety of heterogeneous catalysts have been used for this transformation. For instance, sulfonic acid-functionalized mesostructured silicas have showed excellent activity to convert lower grades of glycerol, such as technical (purity of 91.6 wt%) and crude (85.8 wt%) glycerol in the solketal in 84% and 81%, yields respectively. The catalyst could be reused several times maintaining its activity when refined and technical glycerol were used. However, the high sodium concentration in crude glycerol deactivates the acid sites by cation exchange. This deactivation can be reversed by simple acidification of the catalyst after its use.¹⁸⁴ Ferreira et al.¹⁸⁵ reported the acetalization of acetone with glycerol with good success (98 % selectivity to solketal at near complete conversion) using different heteropolyacids immobilized on silica as catalysts. Mesoporous silicates bearing Lewis acid sites such as Zr-TDU, Hf-TDU, and Sn-MCM-41 also showed excellent activity for performing the acetalization of acetone with glycerol.¹⁸⁶ The

higher activity of these materials compared with commercial zeolites such as Y zeolite, was attributed to the combination of acidity, wide pores, high surface area and higher hydrophobic character than zeolites bearing Bronsted acid sites. More recently different oxides and mixed oxides have been tested as acid catalysts for the acetalization of acetone with glycerol, among them Mo and W-promoted SnO₂,¹³³ TiO₂-SiO₂, mixed oxides¹⁸⁷, niobia¹³⁰ and zirconia and promoted zirconia¹⁸⁸ resulted excellent catalysts able to achieve high selectivity to solketal (80-97%) at near complete glycerol conversion.

The acetalization of glycerol with different aldehydes such as benzaldehyde,¹⁸⁹ furfural,¹³⁴ formaldehyde,¹⁹⁰⁻¹⁹¹ butanal¹⁹² and long chain alkyl aldehydes such as n-heptyl,^{191, 193} n-octyl n-decyl n-dodecyl aldehydes¹⁹³⁻¹⁹⁴ could also produce oxygenate additives for diesel fuels. A variety of homogeneous and heterogeneous Bronsted and Lewis acid catalysts have been used to perform this reaction with different success. Structure of the aldehyde, nature of the catalyst as well as reaction conditions as temperature, the use of solvents, even the presence of water has an important impact on performances. In Table 9 are summarized the recent results on the catalytic preparation of glyceryl acetals. For instance, Deutsch et al.¹⁷⁹ used Amberlyst-36 and Beta zeolite to perform the acetalization of benzaldehyde at chloroform reflux with excellent success (94 % yield). Also good performances were obtained over MoO₃ promoted TiO₂-ZrO₂ in presence or absence of solvent¹⁸⁹(see Table 9). Acetalization of formaldehyde with glycerol was more difficult, particularly in absence of solvent. For instance, with Amberlyst-36 and at reflux of chloroform a maximum yield of 77 % can be achieved¹⁷⁹, however in absence of solvent only 56 % yield of formaldehyde glyceryl acetal could be obtained due to the strong adsorption of the polar reactants on the catalyst surface which deactivate the acid sites.¹⁹¹ Interestingly, when the reaction is performed using formalin (35 %wt aqueous solution of formaldehyde) as a source of formaldehyde, hydrophobic zeolites such a beta zeolite sample synthesized in fluoride media, gives higher yield to formaldehyde glyceryl acetal than Amberlyst-36. This effect was attributed to the lower deactivation rate in presence of water of the hydrophobic beta zeolite.¹⁹¹ Homogeneous Lewis acids such as AuCl₃¹⁹¹ or ZnCl₂¹³⁴ have been used with good success for the acetalization of heptanal and furfural respectively, particularly AuCl₃ resulted an excellent catalyst to perform the acetalization of heptanal in presence of water. This is an interesting point since this oxygenate additive can be obtained with good success

directly from aqueous solutions of glycerol (crude glycerol). Moreover a process has been designed for performing the reactive separation of glycerol in water with n-heptanal, giving a separate phase that contains the acetal in high yields.¹⁹⁵ (Scheme 35)



Scheme 35. Reactive separation of glycerol in water with n-heptanal

Glyceryl acetals of furfural are also obtained in good yield using both homogeneous Lewis acid and heterogeneous Bronsted acid catalysts such as the mesoporous aluminosilicate MCM-41.¹³⁴ Additionally MCM-41 catalyst could be applied to crude glycerol maintaining acceptable yields. The resulting acetals were further hydrogenated followed by acetylation of the free hydroxyl groups, and the resulting mixtures were tested as biodiesel additives.

Table 9. Results of acid catalyzed acetalization of different aldehydes with glycerol

Catalysts	Aldehyde	Solvent	t(h)	T (K)	Yield(%)	Ref.
Amberlyst-36	benzaldehyde	HCCl ₃	4	334	94	179
HBeta (Si/Al=25)	benzaldehyde	HCCl ₃	6	334	94	179
MoO ₃ /TiO ₂ -ZrO ₂	benzaldehyde	Toluene	0.5	388	74	189
MoO ₃ /TiO ₂ -ZrO ₂	benzaldehyde	-	1.5	373	80	189
HBeta (Si/Al=40)	butanal	-	4	343	87	192
USY (Si/Al=30)	butanal	-	4	343	84	192
Amberlyst-36	formaldehyde	HCCl ₃	6	334	77	179
Amberlyst-36	formaldehyde	-	6	373	56	191
Amberlyst-36	formalin	-	8	373	43	191
HBeta(F)(Si/Al= 50)	formalin	-	8	373	68	191
AuCl ₃	formaldehyde	dioxane	4	353	93	191
AuCl ₃	formaldehyde	-	4	353	80	191
AuCl ₃	heptanal	dioxane	0.5	298	93	191
AuCl ₃	Heptanal+ H ₂ O(40 wt%)	-	0.5	353	80	191

ZnCl ₂	furfural	-	0.5	373	90	134
MCM-41	furfural	-	2	373	80	134

5.1.2. Glycerol ethers

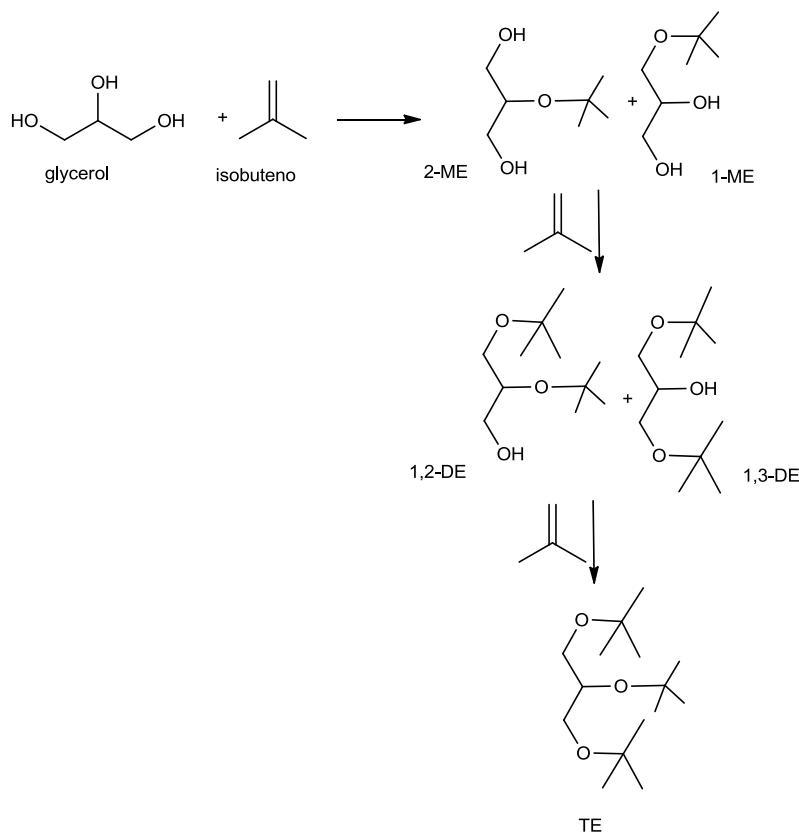
Among the different routes proposed for the production of biofuels from glycerol, the production of ethers has received particular attention. Ethers are obtained by the reaction of glycerol with alcohols (methanol, ethanol, *tert*-butanol) or alkenes. Among them, the etherification of glycerol with *tert*-butanol or isobutene appears promising for the production of mono- (ME), di-(DE) and tri-*tert*-butyl (TE) ethers mixtures. Particularly, di- and tri-ethers are valuable diesel and biodiesel additives due their good blending properties and acceptable cetane number for diesel engine application. Moreover these ethers improve engine performance leading to a reduction in hydrocarbons, carbon monoxide, particulate matter and unregulated aldehydes emission.^{14, 196} They can also act as cold flow improvers in biodiesel reducing its viscosity, and additionally, higher polyethers can also be considered as octane-boosters due its branched alkyl structure and can be an alternative to methyl *tert*-butyl ether¹⁹⁷.

Isobutene is the main O-alkylation agent employed for the production of DE and TE from glycerol, while *tert*-butyl alcohol has been much less utilized due to the formation of water is detrimental for the formation of higher ethers due to de-etherification reactions occur in presence of water.

Etherification takes place as the results of acid catalyzed three consecutive steps with the formation of a mixture o five ethers: two mono-*tert*-butylglycerol ethers (1-ME and 2-ME), two di-*tert*-butylglycerol ethers (1,2-DE and 1,3-DE) and one tri-*tert*-butylglycerol ether(TE) (Scheme 36). Side reactions are the hydration of isobutylene to *tert*-butyl alcohol if water is present in the reaction media, and the oligomerization of isobutylene to C₈ and C₁₂ hydrocarbons.

Homogeneous acid catalysts have been used to obtain mixtures containing high amounts of polysubstitute esters. For instance the ARCO technology,¹⁹⁸ uses *p*-toluenesufonic or

methanesulfonic acid catalysts. However, in this process uneconomic multi-step procedures are needed in order to recover glycerol tert-butyl esters. A variety of heterogeneous catalysts have been tested in the etherification of glycerol with isobutene.¹⁹⁹ Among them, the most utilized have been strong ion-exchange resins such as Amberlyst-15.²⁰⁰⁻²⁰³ For instance, Klepáčová et al.²⁰⁰⁻²⁰¹ performed the solvent free etherification of glycerol with isobutylene or tert-butyl alcohol, catalysed by Amberlyst-15 achieving 100% conversion of glycerol with selectivity to di- and tri-ethers > 92%. However, when tert-butanol was used as alkylation agent a strong deactivation of the catalyst was observed due to the water formed in the reaction deactivated the catalyst. Moreover, it was found that zeolites such as HY and HBeta were not suitable catalysts due to its small pore diameter. The catalytic activity of a commercial HY zeolite has been increased by means of an acid treatment (with citric or nitric acid). This treatment increases the surface area, pore size and pore volume improving the glycerol conversion.²⁰⁴ Thus working at 343 K a selectivity to DE plus TE of 58 % at 85 % glycerol conversion could be achieved. A more acidic resin such as Hyflon® (a perfluorosulfonic ionomer similar to Nafion) is an efficient catalyst to perform the etherification of glycerol with isobutene.²⁰⁵ Hyflon® showed slightly higher performances than Amberlyst-15, achieving 97 % selectivity to DE plus TE at 100 % glycerol conversion, while oligomerization rate on Amberlyst-15 was higher. Moreover, Hyflon® was very stable and could be reused without loss of activity.

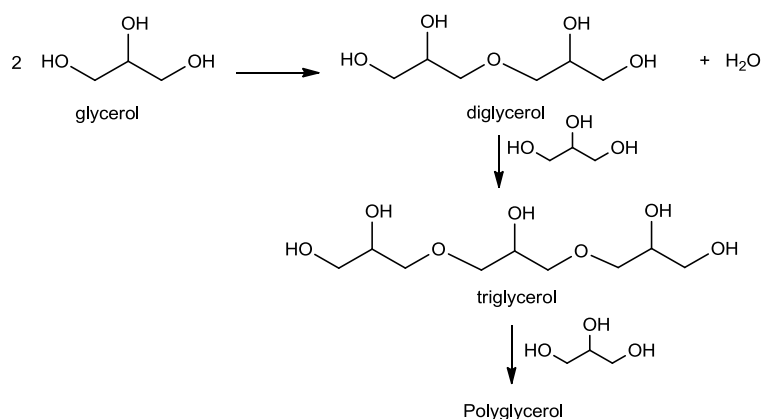


Scheme 36. Etherification of glycerol with isobutene

Melero et al.²⁰⁶ showed that sulfonic-acid-functionalized mesostructured silicas exhibited comparable or even superior catalytic activity to those displayed by the commercial composite nafion-silica (SAC-13). Under optimized reaction conditions, these mesostructured catalysts yield a complete glycerol conversion with selectivity towards di and tri-ethers up to ca. 90% while no formation of undesirable isobutylene oligomers is observed. Gonzalez et al.²⁰⁷ reported recently that microwave-assisted sulfonated SBA-15 catalysts showed higher selectivity toward di- and triethers of glycerol (83-91%) than those sulfonated by conventional heating and much more than Amberlyst-15 (35%). Also microwave-assisted sulfonated silica aerogel gave good selectivity to DE plus TE (75 %) at near complete conversion of glycerol.²⁰⁸

Polyglycerols, specially dyglycerol (DG) and triglycerol (TG) which are produced from the consecutive etherification of two or three glycerol molecules (Scheme 37) are the most important products of the self-glycerol etherification and have found potential applications as fuel additives, as well as other important applications such as in cosmetics, polymers, food additives, surfactants, etc. The control of the polymerization of glycerol for producing short-chain polyglycerols mainly depends on the properties of

the catalysts properties and it is a real challenge. Glycerol can be oligomerized using both acid and basic catalysts. The acid catalyzed etherification of glycerol is a fast process, however it is not selective and leads mainly to higher oligomers (linear, branched, cyclic) along with secondary products coming from dehydration or oxidation processes, therefore base catalysts which are less prone to produce these type of oligomerizations are preferred to perform this reaction.



Scheme 37. Self-etherification of glycerol

In Table 10 are summarized relevant examples on the etherification of glycerol using different homogeneous and heterogeneous base catalyst. Different homogeneous alkali catalysts such as carbonates²⁰⁹⁻²¹⁰ and hydroxides²¹¹⁻²¹² have been used for this transformation, being hydroxides more active than carbonates due to the stronger basicity of the former. In general it is found that using homogeneous base catalysts it is difficult to control the length of the polyglycerol leading to an extensive and non-selective polymerization. In order to increase the selectivity of glycerol self-polymerization micro and mesoporous basic solid catalysts, such as zeolites, MCM-41, alkaline hearth oxides or mixed oxides have been proposed.²¹³ In the case of ion-exchanged zeolites it was found that activity followed the order $X > Y > \text{Beta}$, independent of the alkali ion present. Whatever the catalyst, the selectivity to linear diglycerols was shown to decrease at high conversions. The loss of selectivity with the conversion was attributed to a progressive loss of the microporous structure of the zeolite. Moreover, the instability of the zeolite leads to a slow leaching of alkaline cations, resulting in a coexistence of heterogeneous and homogeneous catalysis.²¹⁴ On the other hand, Cs impregnated on MCM-41 in its siliceous form or with Al were found highly active and selective catalysts. However, collapse of the mesoporous structure

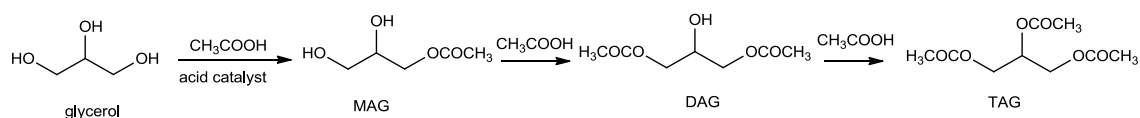
along with leaching of the alkali metal was detected. Alkaline earth metal oxides, have also been used as catalyst for the self-etherification of glycerol. Ruppert et al.²¹⁵ showed that glycerol conversion increased with increasing catalyst basicity; that is, the conversion increases in the order: MgO<CaO<SrO<BaO. It was shown that the catalytic activity was controlled by both basic sites responsible for glycerol deprotonation and Lewis acid sites facilitating dehydration. The best selectivity values for DG plus TG (>90% at 60% conversion) were obtained over CaO, SrO, and BaO. Moreover, it was found that at the beginning of the reaction mainly linear diglycerol was formed, whereas at higher conversion levels branched diglycerol started to form. More recently, Garcia-Sancho et al.²¹⁶ investigated the use of MgAl mixed oxides prepared by coprecipitation and urea hydrolysis as base catalysts for the etherification of glycerol. The highest conversion (50.7%) is found for the catalyst prepared by coprecipitation using NaOH/Na₂CO₃ as precipitating agent. The most selective catalysts for the formation of diglycerols were the samples with the lowest pore diameter, showing shape-selectivity for the formation of diglycerols at low conversions, while negligible amount of leached Mg and Al was detected.

Table 10. Self-etherification of glycerol with different catalysts

Catalyst	m _{cat} (wt%)	T(K)	t(h)	Glycerol Conv(%)	Selectivity (%)		Ref
					DG	TG	
Na ₂ CO ₃	2	533	8	96	24	35	209-210
Na ₂ CO ₃	n.a.	493	n.a.	80	45	36	215
NaOH	2	513	9	63	60	32	211
LiOH	2	513	6	99	33	n.a.	212
NaX (Si/Al=1.1)	2	533	24	100	25	26	214
NaY (Si/Al=2.3)	2	533	24	79	18	8	214
NaBeta (Si/Al= 2.9)	2	533	24	52	44	7.2	214
Cs-MCM-41 _{impregnated} (Si/Al =20)	2	533	16	85	80	22	217
BaO	2	493	20	80	40	40	215
Al-Mg mixed oxide	2	493	24	50	90	10	216

5.1.3. Glycerol esters

Mono-, di- and triacetyl glycerides (MAG, DAG and TAG), also known as mono- di- and triacetin, are obtained from the acetylation of glycerol with acetic acid or acetic anhydride (Scheme 38). These esters have showed a wide range of industrial applications ranging from cryogenics to fuel additives.¹⁷⁵ Particularly di- and triacetin have been introduced in biodiesel formulation in order to improve cold flow and viscosity properties,²¹⁸⁻²¹⁹ moreover they can be used as antiknock additive for gasoline.²²⁰



Scheme 38. Synthesis of mono-, di- and triacetyl glycerides

Acetylation is an acid catalyzed reaction conventionally carried out using mineral acids as catalysts. The formation of di and triacetin is a sequential equilibrium controlled process, and in order to shift the equilibrium towards the desired esters, the acetic acid is used in excess. Due to environmental and economic reasons a variety of solid catalysts able to replace the homogeneous catalysts have been used to perform this reaction. For instance, solid catalysts such as sulfated active carbon²²¹, SO₄²⁻/ CeO₂-ZrO₂,²²² sulphonic resins such as Amberlyst-15,²²³⁻²²⁴ and sulfonic acid functionalized mesostructured materials²²⁵ showed high activity and selectivity towards diacetin and triacetin. However, zeolites and catalysts based on heteropoly tungstate supported on different materials exhibited good conversions of glycerol and high selectivity to mono and diacetin (see Table 11).

Table 11. Acylation of glycerol with acetic acid in presence of different solid acid catalysts

Catalyst	T (h)	T (K)	Glycerol/ acetic acid molar ratio	Glycerol Conv. (%)	Selectivity (%)			Ref
					MAG	DA G	TA G	
Sulfated-AC ^a	3	393	1:8	91	38	28	34	221
SO ₄ ²⁻ / CeO ₂ -ZrO ₂	40	393	1:6	100	3	12	85	188
Amberlyst-15	4.5	383	1:9	97	6	48	45	223
HZSM-5	4.5	383	1:9	86	69	25	6	223
HUSY	4.5	383	1:9	78	73	21	6	223
Sufonic SBA-15	4	398	1:9	78	17	44	39	225
Montmorillonite- K10	0.5	reflux	1:3	96	44	49	5	226
PW/SiO ₂ ^b	7	393	1:16	97	36	59	4	227
25%PW/Nb ₂ O ₃ ^b	4	393	1:5	88	48	47	5	228
PW/Cs-ZrO ₂ ^b	4	393	1:6	95	42	53	5	229
PW/C ^b	3	393	1:16	86	25	63	11	230
WO _x /TiO ₂ -ZrO ₂	3	393	1:6	99	53	40	7	222
Amberlys-36	5	378	8:1	75	93	6	-	231

^aSulfated activated carbon; ^b PW: heteropoly tungstate supported catalysts

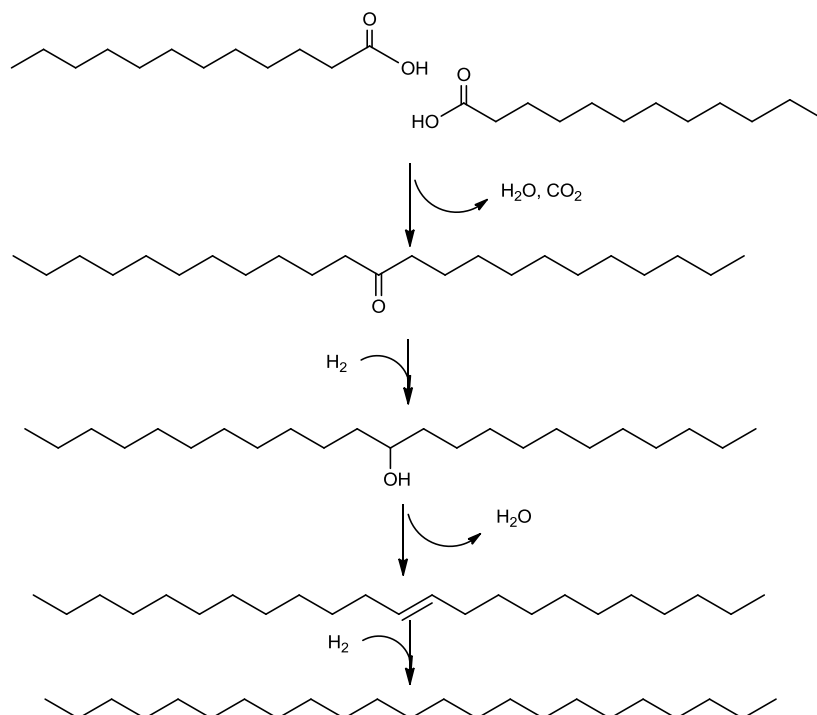
In general it is found that the selectivity to triacetin is limited due to the presence of water which shifts the equilibrium and weakens the catalyst acid strength. Liao et al.²³² have obtained triacetin in 100% selectivity from glycerol with the use of a two-step process in which, glycerol is first reacted with nine fold molar excess of acetic acid in the presence of Amberlyst-35 acid resin. After 4h at 378 K, acetic anhydride is introduced in the reaction medium to complete the acetylation, yielding 100% triacetin. Density functional theory calculations suggest that acetylation with acetic acid is an endothermic process, requiring high energy demand for the introduction of the third acetyl group to form triacetin. In comparison, acetylation with acetic anhydride is exothermic, favoring formation of triacetin.²³³ Indeed, when esterification of glycerol

was carried out using acetic anhydride as acylating agent in the presence of different acid catalysts, HBeta and K-10 montmorillonite gave 100 % selectivity to triacetin at 100 % conversion of glycerol within 20 min working at 333 K and using a molar ratio glycerol/ anhydride of 4.²³⁴ When the molar ratio was reduced to the stoichiometric value (1:3) a decrease in selectivity was observed, although triacetin was still the major product formed. Amberlyst-15 acid resin required longer reaction times, while niobium phosphate gives 100 % selectivity at higher temperatures (393 K).

5.2. Fatty acids as platform for liquid hydrocarbon fuels

The coupling of two carboxylic acid molecules in the presence of a base gives symmetrical ketones.²³⁵⁻²³⁶ When the condensation occurs between two fatty acid molecules, a fatty ketone with $2n-1$ carbon, one molecule of water and one molecule of CO_2 are produced. The ketone can be subsequently hydrogenated to alcohol followed by elimination of water and further hydrogenation of the resultant $\text{C}=\text{C}$, giving alkanes which can be used as diesel fuel or biolubricants. Working in a fixed-bed continuous reactor at 673 K, it was found that MgO was able to produce the ketonization reaction of lauric acid ($\text{C}_{12}\text{H}_{24}\text{O}_2$) with an excellent selectivity to the corresponding ketone (97 % at 95 % conversion). Then, in order to obtain liquid hydrocarbon fuels, a bifunctional catalytic system bearing a hydrogenating function (Pt, Pd, Ru) and basic sites was designed in order to perform a cascade process involving a condensation-hydrogenation-dehydration-hydrogenation sequence (Scheme 39).²³⁷ In order to decrease the reductive decarboxylation of the fatty acid on the metal sites, the process was performed in a two-bed reactor containing in the first catalytic bed MgO and the second bed either a metal/ MgO or a metal/ Al_2O_3 catalyst. Among the different catalytic systems tested, the best results were obtained with the $\text{MgO} + \text{Pt/MgO}$ system, achieving up to 70 % selectivity to n-alkanes at 98.8 % conversion. When Pt supported on alumina was used as catalyst the hydrogenation activity was improved, although due to the acidity of alumina, products containing C_{13} - C_{22} alkanes coming from the hydrocracking of the carbon chain were produced in larger amounts. A total yield of C_{10} - C_{23} n-alkanes c.a. 90 % was obtained with the $\text{MgO} + \text{Pt/Al}_2\text{O}_3$ system. More recently, the same group has performed the ketonic decarboxylation of carboxylic acids with a wide range of molecular weights (from two to eighteen carbon atoms) using ZrO_2 as catalyst. Indeed, MgO presents leaching with time on stream, while this is not the

case for ZrO_2 . Working in a fixed-bed continuous reactor at 673 K full conversion of decanoic acid was obtained with 95 % selectivity towards the desired ketone.²³⁶



Scheme 39. Formation of tricosane from two molecules of lauric acid by ketonization - hydrogenation sequence.

Aalto et al.²³⁸ patented a similar process where the ketonization of fatty acids derived from palm oil were ketonized in a continuous flow reactor using MnO_2 catalyst at 643 K. The ketone was hydrogenated subsequently in a Parr reactor at 600 K using $NiMo/Al_2O_3$ catalyst to obtain C₃₅ linear alkanes in this case useful as lubricants.

Conclusions

We have seen that in the last five years the number of publications and patents on the use of cellulose, hemicelluloses and fatty esters derived products for preparation of fuels and fuel additives has strongly grown. Most used platform molecules include: a) levulinic acid that can be transformed to produce either fuels or additives for fuels; b) Furan derivatives that can also be transformed into fuels and fuel additives; c) polyols to produce liquid fuels as well as oxygenated additives; d) fatty acids for producing diesel and lubricants. The synthesis of liquid fuels in the kerosene and diesel range starting from oxygenated platform molecules described above, the hydrogen to carbon ratio should be increased, while oxygen should be removed. The ideal is to lose the maximum amount of oxygen by means of C-C bond forming reactions by condensation reactions and avoiding decarbonylation reactions with the corresponding loss of carbon. On the other hand in many cases oxygen removal will have to occur by deoxygenation processes that involve C-O bond breaking by means of hydrodeoxygenation catalysts and hydrogen. In some cases the amount of hydrogen required is high and this can have an impact in the final cost. However the development of Shell has brought down the price of natural gas and consequently the price of hydrogen produced by reforming of natural gas. Moreover we have seen that in most cases the processes involve a relatively large number of reaction steps, then an important objective will be to design multifunctional catalyst that can perform cascade type reactions avoiding intermediate product separation and purification. This will be possible provided that multifunctional solid catalysts with the corresponding heterogeneous process were achieved.

In the case of fuel additives, the situation looks easier in the sense that oxygenated products derived from the above platform products can already be used. However, attention should be paid to the fact that the heat power of the additives decreases when increasing the amount of oxygen. Furthermore the formation of too polar additives can present problems due to water solubility in the fuel. What it appears clear is that the reactions involved in fuels and fuel additive production from platform molecules are classical reactions of organic chemistry in where the mechanism of the reaction and catalysts involved are known. However, greener processes should be developed by designing highly efficient solid catalysts able to substitute mineral acids and bases.

Nowadays, commercial processes for the conversion of biomass to fuels are based mainly on the production of biethanol, biodiesel and renewable fuels from gasification and pyrolysis of biomass and hydroprocessing of triglycerides. However, commercial processes based on the catalytic approaches discussed in this review are comparatively scarce. For instance, Avantium (Netherlands) has developed catalytic processes to produce furan derivatives such as ethoxymethylfurfural that can substitute hydrocarbons derived from petroleum. In 2010 Shell and Virent announced the first biogasoline demonstration plant based on Virent's Bioforming® process which converts aqueous carbohydrate solutions into mixtures of hydrocarbons by combining aqueous phase reforming with a modified conventional catalytic process. The aqueous phase reforming step is performed using heterogeneous catalysts and reduces the oxygen content of the carbohydrate feedstock which is subsequently reacted over a Virent modified ZSM-5 zeolite to produce a high-octane gasoline blendstock with an aromatic content similar to a petroleum-derived reformat stream. Virent has trademarked this product BioFormate™. Moreover, the chemical intermediates from the APR step can also be converted into hydrocarbon through a condensation step followed by conventional hydrotreating. (http://www.biofuelstp.eu/catalysis_hydrocarbons.html)

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