PRODUCTION OF 5-(HALOMETHYL)FURFURALS FROM CELLULOSIC BIOMASS AND THEIR SYNTHETIC UPGRADING INTO RENEWABLE CHEMICALS

Thesis

Submitted in partial fulfilment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

by

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DECLARATION

I hereby *declare* that the Research Thesis entitled **“Production of 5-(halomethyl)furfurals from cellulosic biomass and their synthetic upgrading into renewable chemicals”** Which is being submitted to the National Institute of Technology Karnataka, Surathkal in partial fulfilment of the requirements for the award of the Degree of Doctor of Philosophy in **Chemistry** is a *bonafide report of the research work carried out by me*. The material contained in this Research Thesis has not been submitted to any University or Institution for the award of any degree.

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CERTIFICATE

This is to certify *that* the Research Thesis **"Production of 5-(halomethyl)furfurals from cellulosic biomass and their synthetic upgrading into renewable chemicals"** submitted by **Mr. Sharath B. O.** (Registration Number **168007CY16F06**) as the record of the research work carried out by him, is *accepted as the Research Thesis submission* in partial fulfilment of the requirements for the award of degree of Doctor of Philosophy.

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ABSTRACT

The transportation fuels and most of the bulk and fine chemicals are primarily sourced from crude oil. However, the excessive use of crude oil has depleted the reserves, created a disparity between the demand and supply, and degraded the environment. In search of a renewable and preferably carbon-neutral source, biomass has found by many as a commercially-feasible replacement for fossilized carbon. The chemocatalytic valorization of biomass is of particular interest since they are fast, biomass agnostic, selective, and can potentially be integrated into the existing infrastructure. A major challenge in the chemocatalytic value addition of biomass is to develop a new generation of robust, selective, inexpensive, and environment-friendly catalysts that can selectively deconstruct the biopolymers. In this regard, the acid-catalyzed depolymerization and dehydration of biomass-derived carbohydrates (e.g., cellulose) into furanics is an elegant way of removing excessive functionalities from the carbohydrate. Biomass-derived 5-(hydroxymethyl)furfural (HMF), 5-(chloromethyl)furfural (CMF), furfural and levulinic acid (LA) have been used as renewable chemical building blocks for further value addition into fuels and specialty chemicals. In this thesis work, an improved synthesis of CMF and LA have been reported using aqueous HCl as the acid catalyst in the presence of quaternary ammonium chloride as a surface-active agent (SAA). The SAA afforded noticeably higher yields of CMF and LA compared to the control reactions. The reactions were optimized on various reaction parameters such as temperature, duration, loading of the substrate, and the loading of SAA. The SAA was successfully recovered and recycled. LA was converted into alkyl levulinates, a potential diesel additive and a renewable solvent, in the presence of phosphotungstic acid as an environment-friendly and recyclable catalyst. Alkyl levulinates were also prepared by the alcoholysis of CMF and furfuryl alcohol using $HClO_4$-SiO_2 as an inexpensive heterogeneous catalyst. A scalable and high-yielding preparation of 5-(alkoxymethyl)furfural, a novel fuel oxygenate, from CMF has also been reported.

Keywords: Alkyl levulinate, Biofuels, Biomass, Carbohydrates, Catalysis, Green Chemistry, Renewable Synthesis, Surface active agent

CONTENTS

CHAPTER 1: GENERAL INTRODUCTION

CHAPTER 2: LITERATURE REVIEW, SCOPE, AND OBJECTIVES OF THE PRESENT WORK

CHAPTER 3: PHASE TRANSFER CATALYST ASSISTED ONE-POT SYNTHESIS OF 5-(CHLOROMETHYL)FURFURAL FROM BIOMASS-DERIVED CARBOHYDRATES IN A BIPHASIC BATCH REACTOR

CHAPTER 4: CATALYTIC CONVERSION OF BIOMASS-DERIVED CARBOHYDRATES INTO LEVULINIC ACID ASSISTED BY A CATIONIC SURFACE-ACTIVE AGENTS

CHAPTER 5: HIGH-YIELDING SYNTHESIS OF 5-(ALKOXYMETHYL)FURFURALS FROM BIOMASS-DERIVED 5-(HALOMETHYL)FURFURAL (X=Cl, Br)

CHAPTER 6: PREPARATION OF ALKYL LEVULINATES FROM BIOMASS-DERIVED FURFURYL ALCOHOL, LEVULINIC ACID, AND 5-(HALOMETHYL)FURFURAL (X=Cl, Br) USING HOMOGENEOUS AND HETEROGENEOUS CATALYSTS

CHAPTER 7: SUMMARY AND CONCLUSIONS

LIST OF FIGURES

CHAPTER 1

CHAPTER 3

CHAPTER 4

CHAPTER 5

CHAPTER 6

LIST OF SCHEMES

CHAPTER 1

CHAPTER 3

CHAPTER 4

CHAPTER 5

CHAPTER 6

LIST OF TABLES

CHAPTER 3

CHAPTER 4

CHAPTER 5

CHAPTER 6

NOMENCLATURE

HMF	5-(Hydroxymethyl)furfural
CMF	5-(Chloromethyl)furfural
LA	Levulinic acid
SAA	Surface-active agent
TGF	Triglyceride feedstock
FDCA	2,5-Furandicarboxylic acid
PET	Poly(ethylene terephthalate)
^{13}C-NMR	Carbon nuclear magnetic resonance
PEF	Poly(ethylene furanote)
DMF	2,5-Dimethylfuran
XMF	5-(Halomethyl)furfural
BMF	5-(Bromomethyl)furfural
DCE	1,2-Dichloroethane
HCl	Hydrochloric acid
EtOH	Ethyl alcohol
Equiv.	Equivalence
DALA	δ-Aminolevulinic acid
FTIR	Fourier transform infrared
^{1}H-NMR	Proton nuclear magnetic resonance
GVL	γ-Valerolactone
ALs	Alkyl levulinates
ALD	Angelica lactone dimer
EL	Ethyl levulinate
MeOH	Methanol
3-HPA	3-Hydroxypropionic acid
DPA	4,4’-Diphenolic acid
MeTHF	2-Methyltetrahydrofuran
ChoCl	Choline chloride
TLC	Thin layer chromatography

EMF	5-(Ethoxymethyl)furfural
MF	5-Methylfurfural
HPAs	Heteropolyacids
AMF	5-(Alkoxymethyl)furfural
TGA	Thermogravimetric analysis
PXRD	Powder X-ray diffraction
SEM	Scanning electron microscopy
EDX	Energy dispersive X-ray
PTC	Phase transfer catalyst
BTBAC	Benzyltributylammonium chloride
HDTMAC	Hexadecyltrimethylammonium chloride
TBAC	Tetrabutylammonium chloride
BTEAC	Benzyltriethylammonium chloride
DIPEA	N,N-Diisopropylethylamine
TLC	Thin layer chromatography
MMF	5-(Methoxymethyl)furfural
PrMF	5-(Propoxymethyl)furfural
BuMF	5-(Butoxymethyl)furfural
PeMF	5-(Pentyloxymethyl)furfural
HeMF	5-(Hexyloxymethyl)furfural
IpMF	5-(Isopropoxymethyl)furfural
PTA	Phosphotungstic acid
PMA	Phosphomolybdic acid
STA	Silicotungstic acid
ML	Methyl levulinate
BL	Butyl levulinate
FA	Furfuryl alcohol
PL	Pentyl levulinate
PrL	Propyl levulinate
HL	Hexyl levulinate

HPGR	High pressure glass reactor
AcMF	5-(Acetoxymethyl)furfural
aq.	Aqueous
Cat.	Catalyst
org.	Organic
solv.	Solvent
glc	Glucopyranose
PTC	Phase transfer catalyst
BTBAB	Benzyltributylammonium bromide
D	Dextrose
Kd	Dissociation constant

SYMBOLS AND UNITS

wt%	Weight percent
cm	Centimeter
°	Degree
°C	Degree Celsius
δ	Delta
g	Gram
h	Hour
Hz	Hertz
-1	Inverse
λ	Lambda
<	Less than
>	Greater than
L	Liter
MHz	Mega hertz
mL	milliliter
mmol	millimole
K	Kelvin
MPa	Mega Pascal
%	Percent
mol%	Mole percent
min	Minute
M	Molar
ppm	Parts per million
Å	Angstrom
θ	Theta
s	Seconds
γ	Gamma
α	Alpha
β	Beta

CHAPTER 1

GENERAL INTRODUCTION

1.1 PRESENT SCENARIO OF PETROREFINERY

The consumption of crude oil per capita may be used as a yardstick to assess the economic performance of a country (O'Sullivan et al. 2008). At present, transportation fuels and more than 95% of commodity chemicals are primarily sourced from petroleum (Kenworthy 2003). Since the petroleum reservoirs are concentrated in specific geographical locations, the economic survival of many countries like India relies heavily on imported oil (Huber et al. 2006, Nakanishi et al. 2006, Pahwa-Gajjar et al. 2013). With increasing economic activities and rapid urbanization, India's requirement for energy and materials will continue to grow substantially in the coming years, and the crude oil consumption by India is already at par with the major economies in the world (Bhanumurthy et al. 2012). During 2018, India consumed nearly 9.7% of total global crude oil compared to 13.8% by the USA and 6.8% by Japan. Over the past decade, the import of crude oil per day (in thousands of barrels) nearly doubled. **(Figure 1.1)**.

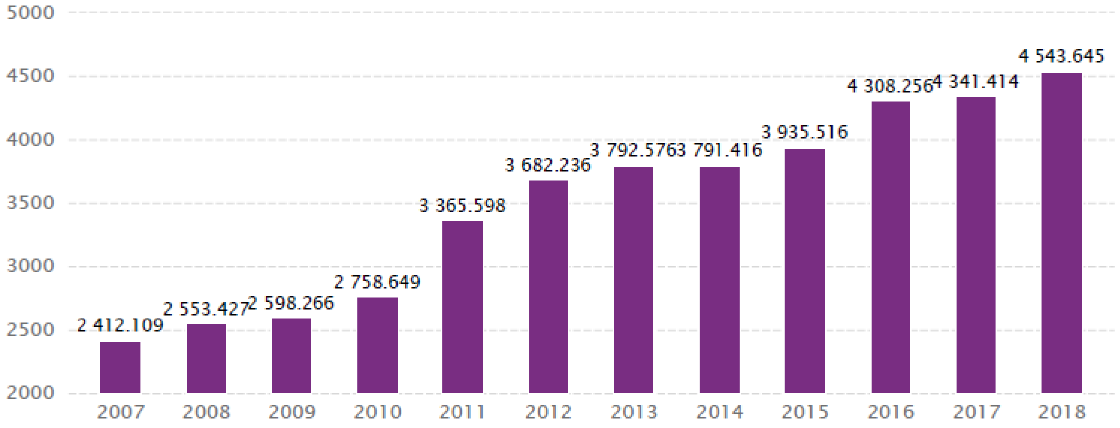


Figure 1.1 Crude oil imports (thousand barrel/day) by India during 2007-2018.

The liabilities involved in importing foreign oil could compromise the economic, socio-political, and foreign policies of a country (Brundtland 1987, Dugmore et al. 2017). Besides, the mass consumption of petroleum-based materials leads to irreversible environmental degradations such as climate shift and global warming (Frumkin et al. 2009, Grant 2011, Huber et al. 2006, Ritchie et al. 2017). It is comforting that significant scientific and technological developments have been made in the direction of ultra-clean and emission-free energies such as solar power and hydrogen fuel cell, which can replace fossilized fuels in the long run (Dincer 2000, Meller et al. 2016).

The ultraclean energy initiatives have been blessed by societal support and strict environmental regulations imposed by governments (Duffield et al. 2006). However, some sectors (*e.g.,* transportation, chemical industries) will likely continue using carbon-based liquid fuels and chemical feedstock in the near future. In this regard, biomass is considered by many as the source of relatively inexpensive, renewable carbon, that has the commercial potential to replace petroleum for liquid fuels and chemicals (Huber et al. 2006, Ragauskas et al. 2006). Carbon-based liquid biofuels, derived from renewable biomass, can be integrated into the existing transportation infrastructure without extensive modifications. The possibility has already been explored by scientists and technologists worldwide. Biodiesel, the methyl- and ethyl ester of fatty acids, can be used as a standalone fuel or as a blend with petrodiesel (Rao et al. 2007). Bio-ethanol, produced by the fermentation of carbohydrates, is currently used as a fuel oxygenate and octane booster in a blend with petro-gasoline (Balat et al. 2008, Dias et al. 2009). However, both biodiesel and bioethanol use only a minute fraction of the total biomass available and their feedstock often compete with the human food supply chain (Dias et al. 2009, Ma et al. 1999, Meller et al. 2016). Furthermore, these fuels suffer from compatibility issues such as the inferior cold-flow properties of biodiesel and the poor oxidative stability of bioethanol (Özçimen et al. 2015). Therefore, there is a relentless search for new generation biofuels that are compatible with the present transportation infrastructure. In a modern biorefinery, energy in the form of heat, advanced biofuels, and biochemicals is produced in an integrated approach starting from abundant and non-food biomass.

1.2 BIOREFINERY VS. PETROREFINERY

Some of the major benefits of the biomass-derived renewable fuels and chemicals are listed below (Cheng et al. 2013, de Jong et al. 2015):

1. Emission of carbon dioxide and other greenhouse gases that are responsible for global warming and climate shift can be abated by switching from petroleum to biomass-derived fuels and chemicals. Biofuels are considered to be carbon-neutral by nature. The source of carbon in biomass is atmospheric CO_2, which became fixed *via*

photosynthesis. The combustion of biofuels releases the CO_2 gas back into the atmosphere completing the carbon cycle. Biomass can be produced within a reasonable time and therefore considered renewable, unlike petroleum.

2. During the processing and combustion of petrofuels, some polluting gases like sulfur dioxide are released inevitably. Biofuels, on the other hand, have inherently low sulfur content (e.g., biodiesel). The addition of biofuels, especially the ones containing oxygen-containing functionalities, often improves the combustion properties of petrofuels. Biodiesel and ethanol require less oxygen during the combustion process and emit fewer particulates.

3. Non-food, lignocellulosic biomass (*e.g.*, agricultural surplus, forestry residues, municipal wastes) are inexpensive and abundant. Utilization of the waste to produce fuels and chemicals is economically competitive and help to mitigate the disposal problems.

4. A large fraction of petrochemicals and materials are non-biodegradable. They accumulate in the ecosystem, causing health and safety issues. Some materials form hazardous intermediates during their degradation process and pose health risks to humans, animals, and aquatic life. New classes of renewable, non-toxic, and biodegradable materials are of immense commercial interest that conform to strict environmental guidelines.

1.3 CLASSIFICATION OF BIOMASS

Biomass is a plant- or animal-based organic matter where the solar energy is stored in the form of chemical energy in the biomolecules such as cellulose or triglyceride that can be released in a controlled fashion to produce usable energy (Ahmed et al. 2012, Corma et al. 2007). Historically, biomass has been in use for centuries as domestic fuel. Biomass is still widely used in the developing economies as a predominant domestic fuel. However, it is mostly combusted in an uncontrolled way that gives low-heating value and pollutes the environment (McKendry 2002). During the past decades, there has been a coordinated effort towards the comprehensive use of biomass into tailor-made fuels and value-added chemicals in a biorefinery (James et al. 2008).

1.3.1 Classification of biomass-based on the origin

The biomass can be broadly classified into three categories based on their source (Maity 2015).

1.3.1.1 Natural biomass

The plant- or animal-based biomasses that are available in nature are called natural biomass. They include the food crops, agricultural and forestry wastes, and animal residues. Each country has a unique set of surplus and inexpensive biomass, which can be used as feedstock for the biorefinery operations (Tumuluru et al. 2011).

1.3.1.2 Residual biomass

These biomasses are produced during various industrial operations. Such as the municipal solid wastes, paper sludge, and sewage. The waste biomasses are of particular interest since they are inexpensive, and their utilization would solve the waste management issues. Therefore, the processes would attract incentives from the government and receive public support (Sanchez et al. 2008).

1.3.1.3 Energy crops

Energy crops are purposefully planted to produce biofuels. The examples include sugarcane in Brazil, corn in the USA, and Jatropha in India. The plants grow fast even in the barren lands with minimal supervision and able to produce more energy per unit weight of biomass when compared to other crops. Some of the important energy crops include switchgrass, miscanthus, bamboo, hybrid willow, silver maple, eastern cottonwood, jatropha, oilseed rape, linseed, algae, and giant kelp. However, they have received only limited success so far as they often use land that would have otherwise used for food crops (Carriquiry et al. 2011, Maity 2015).

1.3.2 Classification of biomass-based on their chemical content

1.3.2.1 Sugar and starchy feedstock

Sucrose, known as table sugar, is a disaccharide made up of a glucose molecule and a fructose molecule. Starch is a polymer of glucose formed by α-1,4 glycosidic linkage. They are abundant in many food crops and grains. Cellulose is the single most abundant biopolymer in the world, which is made of glucose units connected by β-1,4 glycosidic linkage. The terrestrial lignocellulosic and algal biomass are two abundant and inexpensive source of cellulosic biomass (Alonso et al. 2010, Kumar et al. 2011).

1.3.2.2 Triglyceride feedstock (TGF)

Triglyceride is the major component in all organic vegetable oils and animal fats. The fatty acid composition of various oils is unique, and they contain both saturated and unsaturated (mono, poly) fatty acids. The hydrocarbon chains in fatty acids mimic petrodiesel. The methyl- or ethyl esters have been commercialized as biodiesel that can be used as a standalone fuel or more often as an additive to diesel fuel. Apart from the non-food oil crops, there is a significant interest in producing biodiesel from waste cooking oil (Hoekman et al. 2012, Reddy Yenumala et al. 2012).

1.3.2.3 Lignocellulosic feedstock

Lignocellulose is the most abundant terrestrial biomass, and its efficient utilization may reduce global CO_2 emissions (Geboers et al. 2011, James et al. 2010, Meller et al. 2016). Lignocellulose comprises mainly of cellulose (40-50%), hemicellulose (20-40%), and lignin (20-30%) **(Figure 1.2)**. Whereas, extractives like protein and inorganic impurities (i.e., ash) are found in small quantities (Kobayashi et al. 2012, Kumar et al. 2009, Rubin 2008).

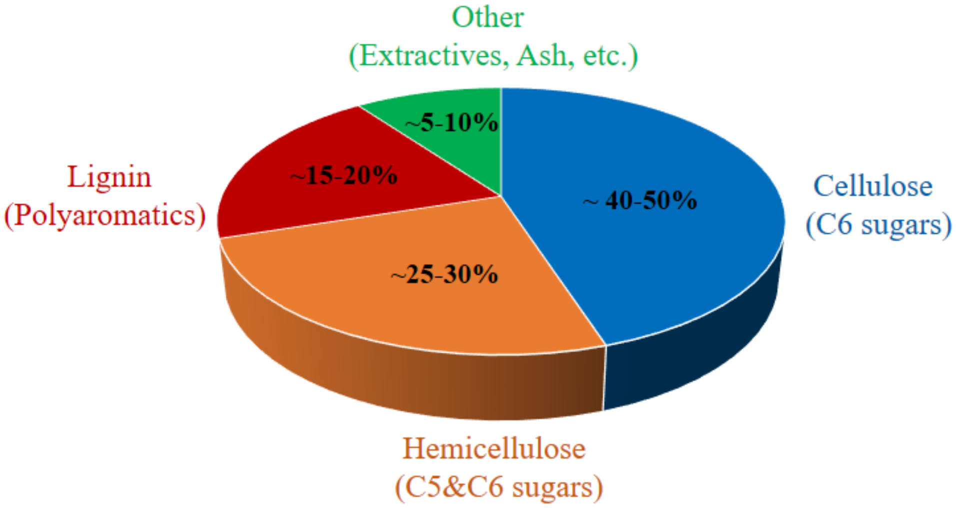


Figure 1.2 Components of terrestrial lignocellulosic biomass.

Cellulose is an abundant linear polymer of β-glucose connected via the β-1,4 glycosidic bonds. The crystalline cellulose is resistant to hydrolysis (Rinaldi et al. 2009). Hemicellulose is an amorphous and branched polymer formed by different sugar units such as glucose, galactose, mannose, xylose, and arabinose. These monosaccharides are linked together by β-1,4 glycosidic bonds and sometime β-1,3 glycosidic bonds. Hemicellulose wraps lignin and cellulose fibers are resulting in a recalcitrant structure (Sheldon 2018). The hydrolysis of hemicellulose is relatively easy compared to cellulose (Saha 2003). The lignin is the most abundant biopolymer composed of aromatic rings connected by ether linkages (Meller et al. 2016, Rosatella et al. 2011, Saeman 1945). Lignin is the primary component in the plant cell wall, providing structural stability and immunity to bacterial and microbial attacks. Selective deconstruction of lignin can be a viable alternative in producing aromatic derivatives directly from biomass (Hamelinck et al. 2005, Whetten et al. 1995). However, the valorization of lignocellulosic biomass has several challenges. For instance, the recalcitrant nature of lignocellulose makes it impervious to most chemicals. Therefore, a pretreatment process is often employed to separate the three major components of lignocellulose and then subject them separately into the chemical-catalytic value addition pathways (Luque et al. 2016). Besides, the biopolymers contain a diverse range of oxygen-containing functionalities. The synthesis of fuels and chemicals out of these would require selective depolymerization and defunctionalization (Simonetti et al. 2008). In the following section, some of the significant biomass conversion technologies were discussed.

1.4 VALUE ADDITION OF LIGNOCELLULOSIC BIOMASS

The relative proportions of cellulose, hemicellulose, and lignin fractions in terrestrial and algal biomass depend on several parameters, including the type of biomass, atmospheric parameters, and storage conditions (Dugmore et al. 2017). The technologies adopted for the value addition depends on the constituents of biomass as well as on the downstream applications of the end product(s). For example, biofuels are high-volume but low-profit products. Feedstock flexibility is generally more important than the product selectivity in preparing biofuels. On the other hand, the production of low-volume but high-profit value-added chemicals demands high selectivity. In this case, the biomass feedstock is routinely pretreated to separate the components of biomass. There are three major technologies, namely, (i) thermolytic, (ii) biotechnological, and (iii) chemocatalytic pathways for biomass value addition (McKendry 2002).

1.4.1 Thermolytic conversion

Thermal deconstruction of the biopolymers leads to a complex mixture of small organics containing a diverse range of structures and functional groups. The energy supplied in terms of heat in the presence or absence of catalyst leads to depolymerization, dehydration, condensation, and various C-C and C-O bond scissions. The process may be classified into three subcategories, namely, gasification, pyrolysis, and hydrothermal liquefaction (Sheldon 2014).

1.4.1.1 Gasification

Heating the solid biomasses around 800-1300 °C under limited oxygen converts them into gaseous products rich in carbon monoxide and hydrogen. The gasification of biomass is a fast and biomass-agnostic process that can be used directly to generate electricity from the heat produced. Alternatively, the gaseous mixture can be purified and subjected to the gas-to-liquid conversion technologies such as the Fischer-Tropsch process (Panwar et al. 2012).

1.4.1.2 Pyrolysis

Pyrolysis is the thermal decomposition of biomass in the absence of oxygen. The pyrolysis product of pyrolysis includes gas, liquid, and a solid char; the proportions of each depend on the reaction parameters (*e.g.*, temperature, pressure, catalyst). Although the thermal process is fast and biomass agnostic in nature, they are almost always non-selective, and a complex mixture of compounds (often unstable) are produced. Therefore, the mixture is primarily used as a fuel for generating energy but not used to make value-added chemicals (Prasad et al. 2018).

1.4.1.3 Hydrothermal liquefaction

Hydrothermal liquefaction of biomass can be carried out in subcritical or supercritical water in the presence of a catalyst. It is a promising method to convert lignocellulosic and algal biomasses with very high moisture content into bio-oil and chemical platforms without requiring energy-intensive pretreatment of the biomass feedstock. The reaction is conducted at moderate temperatures (523-823 K) and pressure (5-25 MPa). In this process, the macromolecules are converted into small molecules of low oxygen content by a combination of dehydration, decarboxylation, and deoxygenation reactions. The yield of liquid fraction is typically high in the process with minimal gas and char formation (Gollakota et al. 2018).

1.4.2 Biotechnological transformation

Biochemical conversions make use of selective enzymatic degradation of the biopolymers into simple molecules by using microorganisms such as native or genetically-engineered bacteria. The microorganisms use lignocellulose as their food and excrete one or more chemicals at the end of their metabolic pathway. The process is highly selective and works under ambient conditions. Many high-value chemicals such as lactic acid and succinic acid are being commercialized using the biochemical pathway. Fermentation of glucose to ethanol is a classic example of the biotechnological value addition of biomass. However, the biochemical conversion technology must follow strict health and environment-safety protocols. In addition, the process requires constant monitoring of the reaction parameters like temperature, nutrients, the concentration of the product, and pH of the reaction broth. The separation of product from the reaction broth is challenging and often detrimental to the microorganisms (Kumar et al. 2016).

1.4.3 Chemocatalytic conversion

The strategy treats the biopolymers in biomass with chemical reagents to transform them into fuels and chemicals. The reactions can be carried out using both stoichiometric reagents and catalytic routes. However, catalytic transformations using inexpensive, robust, selective, and environmentally friendly catalysts are more preferred. Both homogeneous and heterogeneous catalysts have been used for the transformations. These processes are fast, selective, biomass agnostic, and work under relatively milder conditions than thermolytic transformations (Li et al. 2019, Li et al. 2018).

1.4.3.1 Transesterification

Biodiesel is the methyl- or ethyl ester of fatty acids produced by the acid or base-catalyzed transesterification of the triglycerides in oils and fats. Although the first generation biodiesel used oil crops considered as food, the concentration has now been shifted towards non-food oil crops and waste resources (*e.g.*, waste cooking oil). Biodiesel, commercially produced in many countries, including India, can be used as a standalone fuel or as an additive in petrodiesel. Biodiesel is an ultra-low sulfur fuel with good lubricity and cleaner combustion. However, oil-bearing biomasses are only a minor fraction of the terrestrial biomass available, and biodiesel suffers from flow issues in cold climates (Young et al. 2011).

1.4.3.2 Catalytic hydrolysis

The acid-catalyzed dehydration of biomass-derived sugars into renewable chemical intermediates such as furfural, 5-(hydroxymethyl)furfural (HMF), and levulinic acid (LA) was reported more than a century ago (Sheldon 2016, Sudarsanam et al. 2018). The process is an elegant way to defunctionalize and deoxygenate the functionally-diverse and oxygen-rich sugars without carbon-carbon bond scission. For example, the sequential removal of three molecules of water from hexose sugars like glucose forms a molecule of HMF where all the six carbon atoms are retained, but the oxygen content is reduced by 50% (Horvat et al. 1985, Van Putten et al. 2013). In comparison, the fermentation of glucose into ethanol expels 2/3rd of the carbon atoms in glucose as carbon dioxide (Bai et al. 2008, Balat et al. 2008). HMF retains some of the key functionalities of the parent sugar that can be exploited for synthetically upgrading it into fuels and chemicals of commercial significance (Meller et al. 2016). Similarly, the dehydration of pentose sugars like xylose leads to furfural. Furfural is currently commercially produced, and its derivatives have well-established markets (Danon et al. 2014). Rehydration of the furan ring in HMF leads to the formation of a molecule of LA and a molecule of formic acid (Hayes et al. 2006). LA can also be produced from furfural via furfuryl alcohol (An et al. 2018). LA has been listed as one of the top-ten biorenewable chemicals based on its commercial potential (Bozell et al. 2010, Werpy et al. 2004). LA has been used as a renewable chemical building block for several classes of compounds of commercial interests (Sanda et al. 1992).

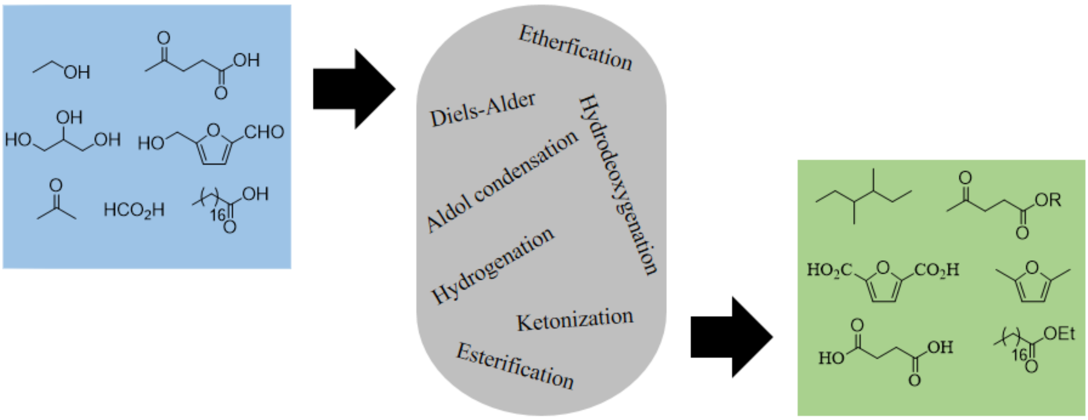


Figure 1.3 Synthetic upgrading of biomass-derived renewable intermediates into fuels and chemicals.

1.5 COMPARISON OF BIOMASS CONVERSION TECHNOLOGIES

	Advantages	Challenges
Thermolytic	The process is fast and biomass agnostic. The gaseous or liquid mixture produced may be used as fuel for generating energy.	The process produces a complex mixture and not suitable for the selective synthesis of value-added chemicals.
Biotechnological	The enzyme-catalyzed processes are very selective and work under ambient conditions. Renewable chemicals or commercial significance such as lactic acid and succinic acid have been synthesized using this strategy.	The process is relatively slow (days), often requires biotechnologically engineered organisms and expensive enzymes. The reaction medium needs to be monitored closely for nutrients, pH, temperature, etc. The recovery of the organism/enzyme is challenging.
Chemocatalytic	The processes are fast, selective, biomass agnostic, and do not require live	Require robust, inexpensive, selective, recyclable, and eco-friendly catalysts. The

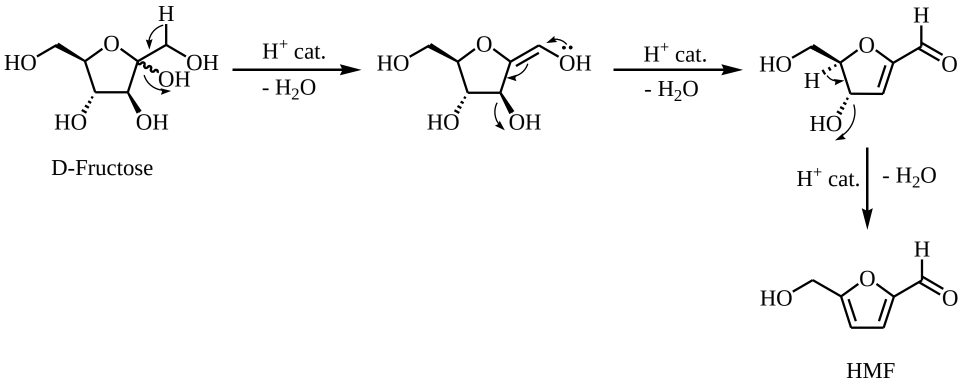
	organisms. They are used to produce both fuels and value-added chemicals.	pretreatment of the biomass is often desired.

1.6 CHEMICAL BUILDING BLOCKS FROM CHEMOCATALYTIC VALUE ADDITION OF BIOMASS

A detailed study on the biomass-derived chemical building blocks or chemical platforms was carried out by Pacific Northwest National Laboratory (PNNL) and National Renewable Energy Laboratory (NREL), USA. This study shortlisted twelve compounds that can be generated from sugars through biological or chemical transformations. The acid-catalyzed hydrolysis of biomass leads to three chemical building blocks, namely, HMF and its congeners, furfural, and LA (Cherubini 2010, Maity 2015).

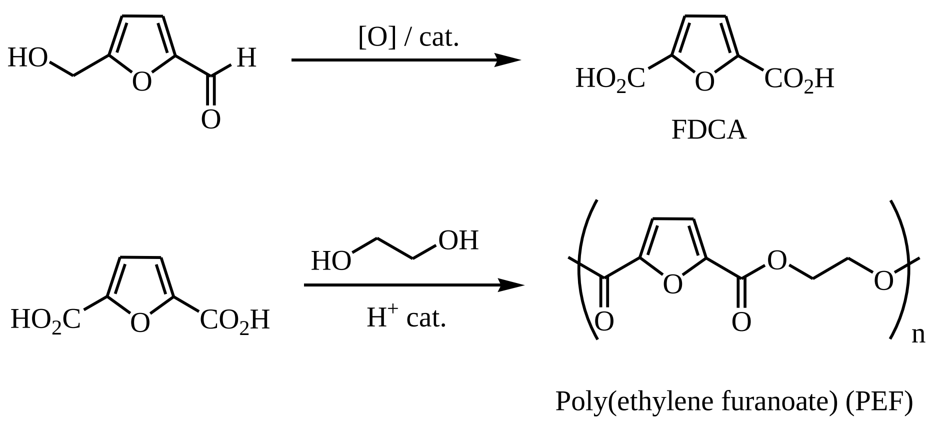
1.6.1 5-(Hydroxymethyl)furfural (HMF)

The sequential removal of three water molecules from hexose sugars like fructose under acid catalysis forms HMF (**Scheme 1.1**). HMF contains an aldehyde and a hydroxymethyl group attached at the C2 and C5 position of the furan ring (Rosatella et al. 2011, S Thombal et al. 2014). The hydrophilic compound has been used as a renewable precursor for the production of a diverse range of products with different levels of complexity, including fuels and fuel additives, monomers, plasticizers, solvents, agrochemicals, and pharmaceuticals (Román-Leshkov et al. 2006, Saha et al. 2014, Van Putten et al. 2013). HMF has been listed as one of the top-ten biorenewable chemicals published by the National Renewable Energy Laboratory (NREL), USA (Davis et al. 2013). The synthesis of HMF was reported as early as 1897 through the acid-catalyzed dehydration of biomass-derived carbohydrates and regained interest in the 1990s (Kuster 1977). Over the past three decades, hundreds of journal publications and patents have appeared in the literature on the preparation and derivative chemistries of HMF as a renewable chemical intermediate. Excellent yields of HMF from simple sugars like fructose have been achieved. However, the production of HMF from inexpensive biomass feedstocks and cellulosic waste products are relatively rare and usually requires special reaction conditions that increase the production cost (Chheda et al. 2007, Mascal et al. 2008). In any case, the hydrophilicity and inherent instability of HMF in aqueous acids complicate the isolation of HMF from the polar reaction media. The isolation and stability issues that continue to plague the HMF chemistry may be alleviated by hydrophobic analogs of HMF such as 5-(halomethyl)furfural (XMF) (Mascal et al. 2009). Other congeners of HMF include ethers, such as 5-(ethoxymethyl)furfural (EMF) and esters like 5-(acetoxymethyl)furfural (AcMF) (Kang et al. 2015). However, the derivatives have their own limitations, often requiring expensive reagents, harsh reaction conditions, and the formation of a large amount of waste.



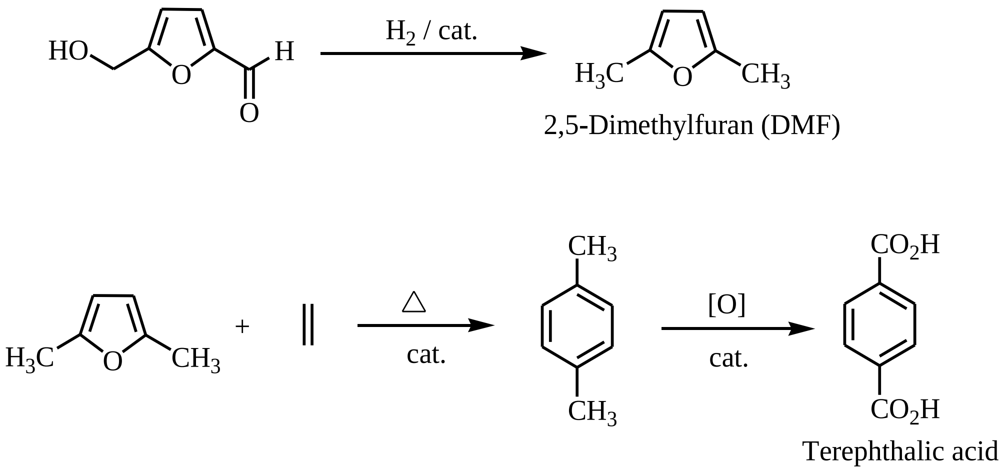
Scheme 1.1 Acid-catalyzed dehydration of D-fructose to HMF.

The three reactive chemical functionalities of HMF, namely aldehyde, hydroxymethyl group, and the furan ring itself have been exploited separately or in combination for various derivative chemistries (Mascal et al. 2014). Together these functionalities undergo various kinds of addition, substitution, oxidation, reduction, and condensation reactions that offer value-added compounds of commercial interest. The most commercially advanced application of HMF is to replace the petrochemical-based poly(ethylene terephthalate) (PET) by a highest-profile bio-based polymer poly(ethylene 2,5-furandicarboxylate) (PEF) as shown in **Scheme 1.2**.



Scheme 1.2 Synthesis of PEF from HMF.

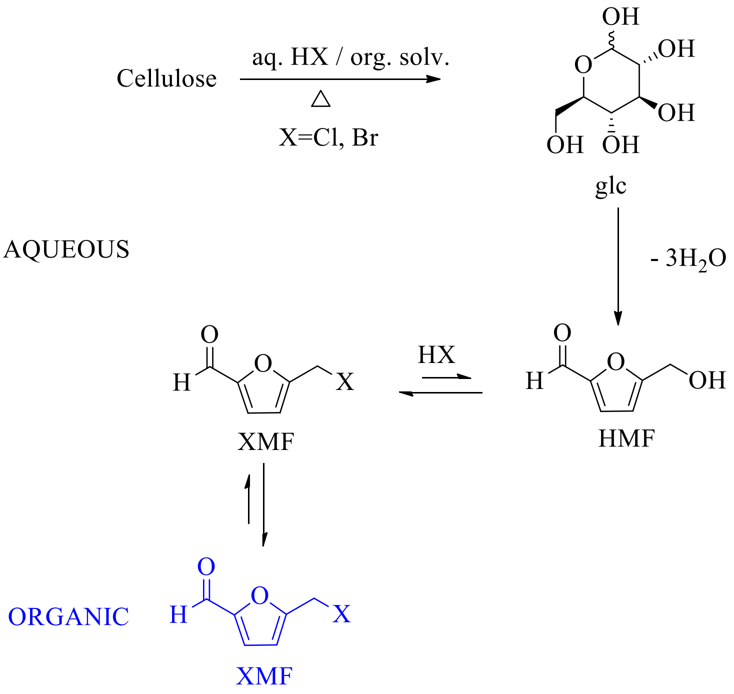
Complete oxidation of both hydroxymethyl and aldehyde functionalities of HMF results in 2,5-furandicarboxylic acid (FDCA). FDCA is used as a precursor for the production of polyethylene furoate (PEF), a renewable alternative to PET. PEF has a lower melting point, higher glass transition temperature, higher tensile strength, and better gas barrier properties, particularly to O_2 permeability than PET. Due to the global demand and superior property of HMF, derivative PEF received worldwide attention from both the academic and industrial communities (de Jong et al. 2012). Caatalytic hydrogenation of HMF forms DMF, a promising biofuel whose physicochemical properties closely match those of gasoline. It is also a high-value chemical intermediate for making renewable *p*-xylene, an entry-point for bio-based terephthalate polymers (Thananatthanachon et al. 2010) (**Scheme 1.3**).



Scheme 1.3 Synthesis of terephthalic acid from HMF.

1.6.2 5-(Halomethyl)furfural (XMF)

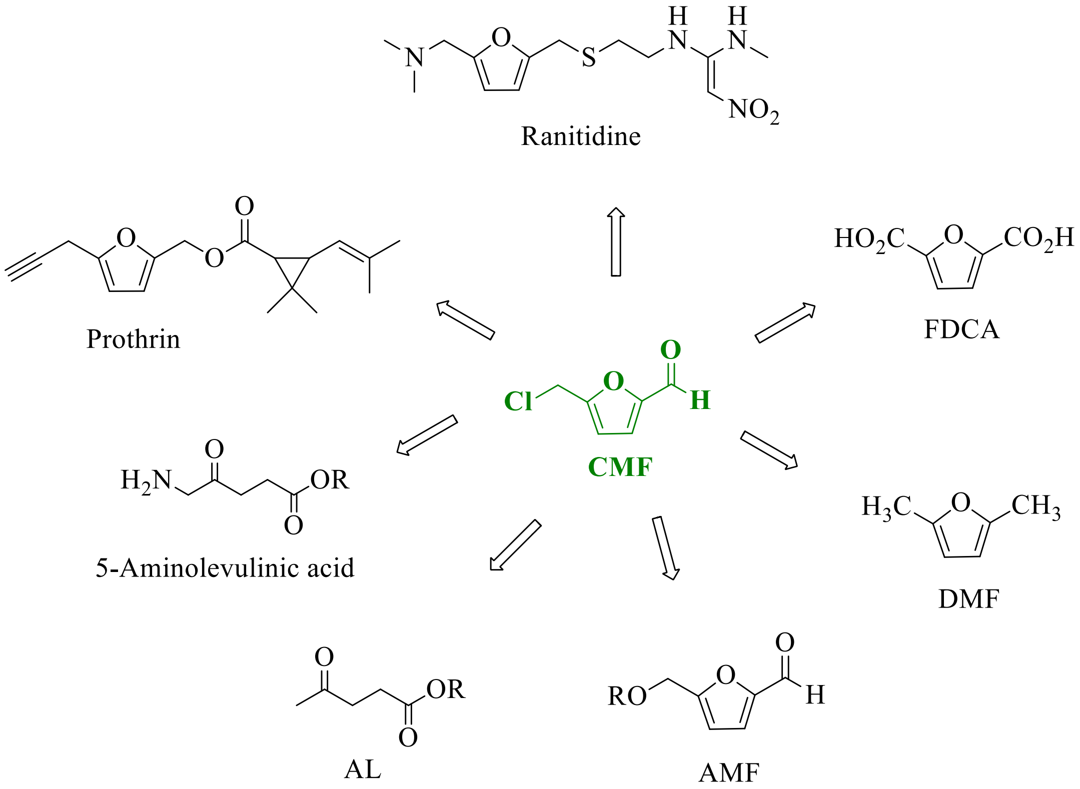
XMF is an organic compound with formula $C_6H_5O_2X$ (X=Cl or Br). XMF is a congener of HMF wherein a halomethyl group replaces the hydroxymethyl group. XMF can be derived from sugars, cellulose, or lignocellulosic biomass. The better leaving group ability of the halide ion (compared to hydroxide) makes XMF reactive towards a plethora of reactions such as nucleophilic substitution, which facilitates the conversion of XMF to various value-added chemicals (Mascal 2019). The 5-(iodomethyl)furfural is only stable in solution and could not be isolated. The 5-(fluoromethyl)furfural is also known but less studied owing to its diminished reactivity (Mascal et al. 2014). A literature search on the SciFinder® showed only 218 references on CMF against a whopping 13797 references on HMF. CMF, unlike HMF, is hydrophobic and can be isolated conveniently from the aqueous reaction media by simple solvent-solvent extraction. CMF can potentially participate in all derivative chemistries of HMF (Girisuta et al. 2006). Which includes Bio-Fuels, renewable polymers, specialty chemicals, value-added agrochemicals, and pharmaceutical products (Mascal et al. 2014). The first synthesis of 5-(chloromethyl)furfural (CMF, X=Cl) and 5-(bromomethyl)furfural (BMF, X=Br) was reported by Fenton and Gostling by treating the cotton with ethereal hydrogen chloride or hydrogen bromide (Fenton et al. 1899, 1901). In 1944 Haworth and Jones first reported the synthesis of CMF from sucrose using biphasic acid/solvent reaction; they got 21% isolated yield of CMF. Over the past decades, synthesis of CMF from carbohydrates and cellulosic biomasses have been achieved with varying degrees of success. CMF and 5-(bromomethyl)furfural (BMF) are of many interests since they can be synthesized by simply treating the carbohydrates and cellulosic biomasses with gaseous or concentrated aqueous HX (X=Cl, Br). Being significantly more hydrophobic compared to HMF, CMF and BMF can be conveniently separated from the aqueous reaction mixture by solvent-solvent extraction. According to the mechanistic details, acid-catalyzed dehydration of sugars forms HMF. Protonation of the -OH group in HMF, followed by nucleophilic substitution by the halide ions, forms XMF (X=Cl, Br). CMF and BMF are hydrophobic, which can easily extract into the organic layer as soon as it forms and sheltered from further aqueous acid-promoted decompositions (Mascal 2019) **(Scheme 1.4)**.



Scheme 1.4 Formation of CMF and BMF in an aqueous-organic biphasic reaction.

Over the past decades, synthesis of CMF from carbohydrates and cellulosic biomass has been achieved with varying degrees of success. In 2008, Mascal et al. reported the synthesis of CMF from various carbohydrates and cellulosic biomass in a biphasic batch reactor containing aqueous HCl and 1,2-dichloroethane (DCE) in the presence of LiCl as an additive. The reaction was conducted at 65 °C, and the aqueous layer was continuously extracted by DCE for 30 h. The procedure yielded CMF along with HMF, LA, and 2-(2-hydroxyacetyl)furan (Mascal et al. 2008). In a later report, the selectivity and yield of CMF were improved significantly by performing the reaction in a glass pressure reactor. The sealed reactor permitted reaction temperature (ca. 90 °C) higher than the boiling point of DCE and without evaporative loss of HCl gas during the reaction. The reaction completed within 3 h and CMF was isolated in yields as high as 88%. However, the process required intermittent extraction of DCE, and the total volume of DCE used per mole of CMF was high. In the above process, LA was co-produced as a minor product (Mascal et al. 2009). In 2013, Gao et al. reported the preparation of CMF in a biphasic open batch reactor containing a mixture of HCl (37%) and H_3PO_4 (85%) as the aqueous phase and chloroform as the extracting solvent. The reaction was conducted at 45 °C for 20 h (Gao et al. 2013).

The derivative chemistry of CMF follows two essential reaction manifolds, namely furanic and levulinic. The hydrolysis of CMF or BMF in boiling water produces HMF and LA in excellent yields under optimized conditions (Mascal et al. 2010). CMF on catalytic hydrogenation produces 2,5-dimethylfuran (DMF), which acts as a chemical feedstock for the synthesis of biorenewable *p*-xylene (Cheng et al. 2015, Hulea 2018, Karakhanov et al. 2018, Maneffa et al. 2016). Like HMF, the oxidation of CMF provides FDCA for the synthesis of renewable polyesters like PEF (Papageorgiou et al. 2014). CMF has been used as a precursor for the synthesis of Ranitidine, a blockbuster drug to treat gastric and duodenal ulcers (Mascal et al. 2011, Katsuda et al. 1969). CMF has been transformed into δ-aminolevulinic acid (DALA), a promising photodynamic therapy drug and natural herbicide, in three efficient steps. Prothrin, a furan-based pyrethroid, has also been synthesized from CMF **(Scheme 1.5)**.



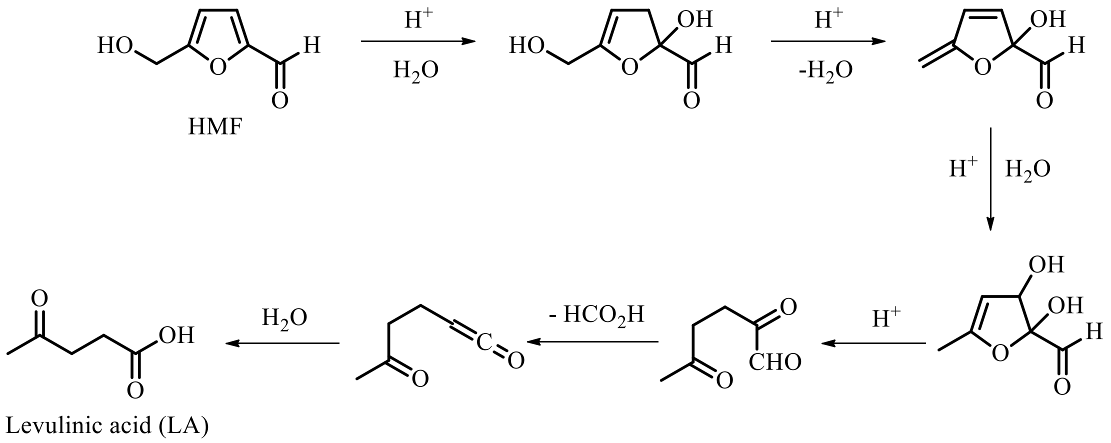
Scheme 1.5 Derivative chemistries of CMF.

1.6.3 Levulinic acid (LA)

4-Oxopentanoic acid or levulinic acid (LA) is a colorless, crystalline, low-melting (m.p. 33-37 °C) solid and has a boiling point of 246 °C (Bozell et al. 2010). LA is believed to form alongside a molecule of formic acid by the rehydration and ring-opening of HMF. The first synthesis of LA was reported in the 1840s by Dutch Professor G. J. Mulder by heating sucrose with mineral acid at high temperatures (Climent et al. 2014). Over the past decades, hundreds of journal publications and patents have been attributed to the production and downstream applications of LA. LA is a synthetically versatile molecule having two highly reactive functionalities (*i.e.,* ketone & carboxylic acid). LA has been used as a renewable chemical intermediate for the synthesis of a range of value-added compounds such as fuels, fuel additives, fragrances, solvents, pharmaceuticals, and plasticizers (Christensen et al. 2011, Pileidis et al. 2016, Zhang 2016). LA was listed by NREL, USA, as one of the top-ten renewable chemicals with commercial implications.

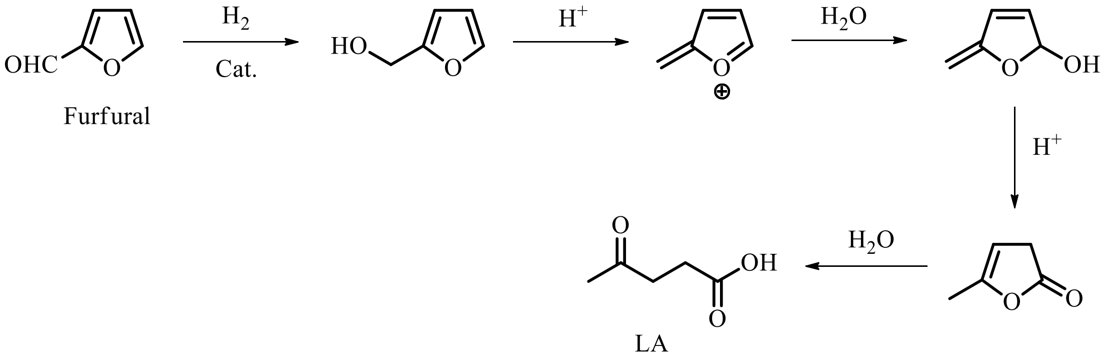
LA is a γ-ketocarboxylic acid that can be sourced from both hexose and pentose sugars. LA is known to form by the ring-opening of the HMF intermediate **(Scheme**

1.6). There are several high-profile reviews on the production of LA from various biomass-derived sugars, carbohydrates, and even untreated biomass feedstocks (Werpy et al. 2004). An acid of some sort are routine used that range from mineral acids, organic acids, metal salts, zeolites, acidic resins, ionic liquids, and supercritical fluids (Ren et al. 2013). Some of the recent literature on the production of LA from biomass are listed in the literature review.



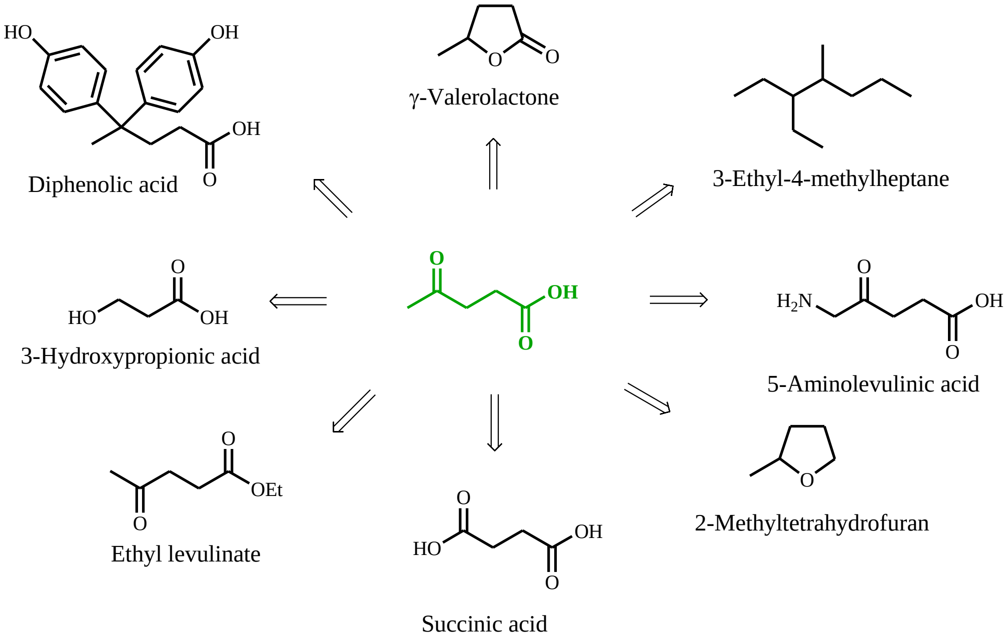
Scheme 1.6 Mechanism of the formation of LA from HMF.

LA can also be sourced from C5 sugars through the furfural intermediate **(Scheme 1.7)**. Furfural is catalytically hydrogenated into furfuryl alcohol. The acid-catalyzed ring-opening of furfuryl alcohol leads to LA after a series of protonation and hydration steps.



Scheme 1.7 Mechanism of the formation of LA from furfural.

The derivative chemistries of LA are somewhat complementary to those of HMF (or CMF). The acid-catalyzed intramolecular lactonization of LA, followed by catalytic hydrogenation, leads to γ-valerolactone (GVL) (Antonetti et al. 2016). GVL has received serious attention as a renewable solvent and fuel additive. GVL can be decarboxylated into butenes, which then can be oligomerized into gasoline-like branched hydrocarbon fuels. LA has also been converted into C7-C10 branched hydrocarbons in three steps. In the first step, the intramolecular lactonization of LA led to angelica lactones (a mixture of two isomers). In the second step, AL was dimerized using K_2CO_3 as a base catalyst. The angelica lactone dimer (ALD) was then hydrodeoxygenated into gasoline-like molecules with 3-ethyl-4-methylheptane as the major product. In a later report, the hydrodecarboxylation of ALD led to a hydrogen-economic synthesis of branched hydrocarbons such as 3,4-dimethyl hexane. The Fischer esterification of LA with monohydric alkyl alcohols lead to alkyl levulinates (ALs) (Al-Shaal et al. 2015, Mascal 2019). ALs such as ethyl levulinate (EL) are novel fuel oxygenate and green solvent. ALs can also be prepared by reacting angelica lactones with alcohol (Zhao et al. 2015). Bio-succinic acid is considered a '*sleeping giant'* for its huge commercial potential as a renewable and biodegradable monomer for new-generation polymers. Selective Baeyer-Villiger oxidation of LA by aqueous H_2O_2 using trifluoroacetic acid as an acid catalyst formed succinic acid in good isolated yield. The selectivity of the oxidation of LA changed in the basic medium and led to the formation of 3-hydroxypropionic acid (3-HPA). 3-HPA can be used as a monomer, or it can also be transformed into acrylic acid by acid-catalyzed dehydration (Pileidis et al. 2016).



Scheme 1.8 Derivative chemistries of LA.

Acid-catalyzed condensation of LA with two moles of phenol leads to the formation of 4,4’-diphenolic acid (DPA). DPA has been proposed as a greener replacement for Bisphenol-A in various polymeric applications. Selective hydrogenation of LA over various noble-metal-based homogeneous and heterogeneous catalysts leads to 2-methyltetrahydrofuran (MeTHF). MeTHF has potential applications as a renewable solvent, fuel oxygenate, and as a renewable chemical intermediate for other specialty chemicals. LA has also been used as a starting material for the synthesis of δ-aminolevulinic acid (DALA). DALA is a well-known photodynamic therapy drug, as well as a natural herbicide of low mammalian toxicity. The synthesis starts with the selective bromination of LA in the 5-position.

CHAPTER 2

LITERATURE REVIEW, SCOPE, AND OBJECTIVES OF THE PRESENT WORK

2.1 Literature review of 5-(halomethyl)furfural (XMF)

The following literature review provides a brief account of the challenges towards the chemical catalytic valorization of biomass-derived carbohydrates into value-added chemical intermediates and their synthetic upgrading into renewable fuels and specialty chemicals. Mascal (2019) reviewed the preparation of CMF from carbohydrates and cellulosic biomasses. CMF has been demonstrated as a biomass-derived renewable chemical intermediate for the synthesis of a wide range of products of commercial interests including hydrocarbon fuels, fuel oxygenates, monomers for polymers, agrochemicals, and pharmaceuticals. The review discussed the efficient production of CMF from carbohydrates and untreated cellulosic biomass samples under relatively straightforward and mild conditions. Given the hydrophobic character, CMF could be isolated conveniently from the aqueous HCl using solvent-solvent extraction. The review critically evaluated the relative advantages and disadvantages of using HMF and CMF as a renewable chemical platform for further value addition pathways.

Substrate	Reaction Conditions	Product	Yield (%)	Reference
Cellulose	HBr-diethyl ether, 15 °C, 24 h	BMF	28	(Fenton et al. 1899)
	HCl-diethyl ether, 15 °C, 24 h	CMF	9	
D-Fructose	aq. HCl, $MgCl_2.6H_2O$, QACLTAC, 85 °C, 4 h	CMF	65	(Hamada et al. 1982)
D-Fructose	DMF/SPC-108 (H^+)/MIBK, $POCl_3$, TCE, 80 °C, 12 h	CMF	80	(Sanda et al. 1992)
Cellulose	aq. HCl-DCE, LiCl, 65 °C, 30 h	CMF	71	(Mascal et al. 2008)

Cellulose	aq. HCl-DCE, 100 ℃, 4 h	CMF	78	(Mascal et al. 2009)
D-fructose	H_2SO_4, DMA-LiBr, 100 ℃, 5 h	HMF	92	(Binder et al. 2009)
	H_2SO_4, DMA-LiI, 100 ℃, 5 h		89	
D-fructose	aq. HCl-DCE, 100 ℃, 60 s	CMF	76	(Brasholz et al. 2011)
Cellulose	aq. HBr-Toluene, LiBr, 65 ℃, 48 h	BMF	80	(Kumari et al. 2011)
Glucose			50	
D-Fructose			82	
Sugarcane Bagasses	$AlCl_3$, 85 °C, 3 h	CMF	72	(Chen et al. 2012)
D-Fructose	4/1 HCl/H_3PO_4, $CHCl_3$, 45 ℃, 20 h	CMF	47	(Gao et al. 2013)
Glucose	aq. HCl-DCE, 70 ℃, 15 min	CMF	39	(Breeden et al. 2013)
Glucose	aq. HBr-DCE, LiBr, 65 ℃, 24 h	BMF	64	(Bredihhin et al. 2013)
Glucose	$CrCl_3$/HCl, $CHCl_3$, 45 ℃, 10 h	CMF	14	(Wu et al. 2015)
D-Fructose			62	
Sucrose			72	
Cellulose			6	
Glucose	aq. HCl-DCE, 79 ℃, 30 min	CMF	30	(Lane et al. 2016)

Cellulose	aq. HCl (10 M), DCE, 110 °C, 3 h	CMF	82	(Meller et al. 2016)
	aq. HBr (8.5-9 M), DCE, 95 °C, 3 h	BMF	74	
RSC	aq. HCl-DCE, 100 °C, 1 h	CMF	63	(Zhang et al. 2017)
FCCS			43	
D-Fructose	$AlCl_3.6H_2O$/ChCl-MIBK, 120 °C, 5 h	CMF	50	(Zuo et al. 2016)
Inulin			23	
Sucrose			18	
Glucose			17	
D-Fructose	$Al_2(SO_4)_3$/ChoCl, MIBK, 120 °C, 5 h	BMF	50	(Le et al. 2017)
D-Fructose	aq. HCl-DCE, 100 °C, 1 min, continuous flow reactor	CMF	74	(Kohl et al. 2017)
Sucrose	aq. HCl-DCE, 100 °C, 2.5 min, continuous flow reactor		50	
HFCS	aq. HCl-DCE, 100 °C, 1.5 min, continuous flow reactor		85	

Abbreviations: QACLTAC: quaternary ammonium chloride-lauryltrimethylammonium chloride, MIBK: Methyl isobutyl ketone, DCE: 1,2-Dichloroethane, ChoCl: Choline chloride, HFCS: High Fructose corn syrup, RCS: Reference corn stover, FCCS: Forage chopped corn stover.

Fenton et al. (1899) reported the first synthesis of BMF by treating biomass-derived carbohydrates with diethyl ether saturated with hydrogen bromide gas. The reaction was conducted at 15 °C for 24 h, and BMF was isolated in a 28% yield starting from cellulose. In 1901, the same method was used for the synthesis of CMF by treating cellulose with hydrogen chloride gas dissolved in diethyl ether.

Hamada et al. (1982**)** studied the effect of surface-active agents on the conversion of sugars into CMF. The reaction was carried out in an aqueous HCl and toluene biphasic reactor starting from D-fructose, $MgCl_2.6H_2O$, and a catalytic amount of surface-active agent QACLTAC (quaternary ammonium chloride-lauryltrimethylamminium chloride). The reaction was performed at 85 °C for 4 h, and CMF was isolated from the toluene layer in 65% yield.

Sanda et al. (1992) reported a two-step synthesis of CMF from fructose in a three-phase system (DMF/SPC 108 (H^+)/MIBK). In the first step, dehydration of fructose into HMF was carried out at 80 °C using Lewatit SPC 108 (H^+) as the acid catalyst and the combination of *N*,*N*-dimethylformamide (DMF) and methyl isobutyl ketone (MIBK) as the solvent system. The HMF was then treated with a solution of phosphorylchloride at room temperature for 5 h to get CMF in an 80% overall yield.

Mascal et al. (2008) reported the synthesis of CMF from various carbohydrates in an aqueous HCl-DCE biphasic open batch reactor using continuous extraction. The aqueous medium consisted of concentrated (35%) HCl and LiCl (5 wt%) as additive. The reaction was conducted at 65 °C for 30 h. Cellulose produces around 71% yield of CMF and a small number of related furans like HMF, HAF, and LA, bringing the total carbon yield of 85-91%. Glucose and sucrose provided CMF and other furanics with a combined yield of 95%. CMF was also converted into biofuels like EMF and 5-methylfurfural (MF).

Mascal et al. (2009) reported the preparation of CMF in a closed biphasic batch reactor consisting of 35% aq. HCl and DCE. The reaction was conducted in a glass pressure vessel under conventional heating and magnetic stirring. The DCE layer containing CMF was removed at regular intervals, and fresh DCE was introduced. The one-pot process afforded CMF in excellent selectively and high isolated yield (70-90%) from carbohydrates as well as lignocellulosic biomass such as corn stover. LA formed as a minor product (5-9%) and isolated from the aqueous layer.

Binder et al. (2009) reported the one-pot synthesis of HMF from biomass using LiCl in *N*,*N*-dimethylacetamide (DMA). The results revealed that DMA-LiCl acts as a medium to dissolve biomass-derived cellulose without modifying its chemical structure. In addition, the formation of macrocations of DMA. Li^+, as a result of Li^+ ions association with DMA, enhanced the concentration of weakly ion-paired halide ions. These halide ions dramatically influence the HMF yield by forming a stable intermediate. Further, the effect of halide additives on HMF yield was examined using fructose as the substrate and H_2SO_4 as the catalyst. Among the examined halide additives, bromide and iodide ions are more effective as ionic additives, exhibit superior nucleophilicity and yielded 92 and 89% HMF (100 °C, 4 h), respectively from fructose.

Brasholz et al. (2011) reported the production of HMF, CMF, and LA from biomass-derived sugars in a flow reactor. When the reaction was carried out at 100 °C with a residence time of 60 s and dichloromethane as the extracting solvent, CMF was isolated in a 76% yield from fructose. Sucrose and glucose provided CMF in around 50% yield. The authors also reported the derivatization of CMF both in batch and flow conditions. For example, CMF was oxidized to FDCA by aqueous nitric acid in a batch reactor.

Kumari et al. (2011) described the production of BMF from cellulose in aq. HBr (55%)-toluene biphasic batch reactor using LiBr as an additive. The reaction was conducted for 48 h at 65 °C under constant mechanical stirring. Cellulose provided an 80% yield of BMF, whereas glucose and fructose provided 50% and 82%, respectively. The mechanistic study on the formation of BMF from cellulose was explained. BMF was converted into EMF and HMF in quantitative yields.

Chen et al. (2012) reported the one-pot conversion of sugarcane bagasse into CMF using various alkali, alkaline earth, and transition metal chlorides ($AlCl_3$, $MgCl_2$, etc.). Among the metal chloride catalysts studied, $AlCl_3$ showed an excellent catalytic efficiency towards the formation of CMF from bagasse. The reaction was optimized on the reaction temperature, time, and the loading of $AlCl_3$. CMF formed in 72% yield when the reaction was conducted at 85 °C for 3 h.

Gao et al. (2013) reported the production of CMF in a biphasic batch reactor using chloroform as the extracting solvent and the combination of aqueous HCl (35%) and orthophosphoric acid (85%) as the catalyst. The reaction was carried out at 45 °C for 20 h using conventional heating and magnetic stirring. CMF was isolated in 47% yield from fructose but only 7 and 8% yield from glucose and cellulose, respectively. The effect of various organic solvents and the molar ratio of HCl and H_3PO_4 were examined on the yield of CMF. Chloroform was found to be the most effective extracting solvent, and 4/1 molar ratio of aq. HCl and aq. H_3PO_4 was found to be the optimum value.

Putten et al. (2013) published a comprehensive review of the production of HMF from various simple sugars, polymeric carbohydrates, and lignocellulosic biomasses using various homogeneous and heterogeneous acid catalysts. Homogeneous catalysts included mineral acids, water-soluble organic acids, ionic liquids, and HPAs. Heterogeneous acids examined include metal salts, mineral acids supported on various supports, and sulfonated resins. Special reaction conditions included the use of various additives, supercritical fluids, and ionic liquids under conventional and microwave heating. Detailed mechanistic detail for the formation of HMF was provided. Various derivative chemistries of HMF were discussed, and their potential markets were highlighted.

Breeden et al. (2013) reported the production of CMF from biomass-derived sugars using microwave heating in a biphasic (aq. HCl/DCE) reaction system. CMF was isolated in 39% yield within 15 min at 70 °C from glucose. The effect of substrate loading, reaction temperature, and duration of the reaction was examined on the yield of CMF. Furthermore, a decrease in the yield of CMF was observed with increased substrate loading.

Bredihhin et al. (2013) reported the conversion of carbohydrates and biomass into BMF in an aq. HBr-DCE biphasic reaction medium using at 65 °C using LiBr as an additive. The typical reaction procedure involves the frequent separation of the DCE layer after 1, 2, 3, and 24 h, and BMF was isolated in 64% yield from glucose. The authors also examined this method for the production of BMF directly from the different wood species. For example, dry aspen provided a BMF in 55% yield.

Wu et al. (2015) described that metal chloride assisted the one-pot synthesis of CMF in the biphasic (HCl-$CHCl_3$) batch reactor. Glucose was used as the model substrate, and the reaction was performed at 45 °C for 10 h. The authors studied the effect of various metal chlorides as an additive on the yield of CMF. Among the various metal chlorides studied, $CrCl_3$ gave 14% yield of CMF from glucose. Whereas $CrCl_3$ afforded 62%, 72%, and 6% yield of CMF from fructose, sucrose, and cellulose respectively, $ZnCl_2$ afforded 53%, 52%, and 4% yield of CMF from the same substrates under identical reaction conditions.

Lane et al. (2015) described the production of CMF from glucose in a biphasic reactor. CMF was produced in a 30% yield using 6 M HCl within 30 min at 79 ℃. The authors studied the efficiency of various organic solvents for extracting CMF from the aqueous reaction medium. Among the solvents examined, DCE was found to be the most efficient extracting solvent. Furthermore, the reaction was optimized on the reaction temperature, time, stirring rate, and substrate loading.

Meller et al. (2016) described the synthesis of CMF and BMF from cellulose in both open and closed batch reactors. The effect of reaction temperature, the substrate to solvent ratio, acid concentration, and reaction time on the yield CMF and BMF were studied. In a closed system, 82.6% CMF was obtained within 3 h at 110 ℃ using 10 M HCl. In comparison, the CMF yield was only 9.4 % in an open reactor when the reaction was conducted at 70 ℃ for 8 h. A marked difference in the yield of CMF was attributed to the higher temperatures attainable in a closed reactor without outgassing HCl or evaporative loss of the solvent. Analogously, BMF was obtained in nearly 74% yield from cellulose when the reaction was conducted at 95 ℃ for 3 h using 8.5-9 M HCl, whereas only 59.5 % BMF was obtained in an open reactor. In addition, the closed reactor did not require LiX (X=Cl, Br) salts as an additive and required less use of organic solvent.

Zhang et al. (2017) reported a hydrochloric acid-catalyzed one-pot production of CMF from biomass-derived reference corn stover (RSC) and forage-chopped corn stover (FCCS). In the typical reaction, RSC and FCCS (10% w/v) were dissolved in biphasic medium HCl/DCE (2:1 volume basis) and reacted at 100 °C for 1 h. CMF was obtained in 63% and 43% yield from RSC and FCCS, respectively. The parametric study revealed that the particle sizes of FCCS affect the yield of CMF, and larger particles (ca. >19 mm) reduced the CMF yield from 43 to 35%. The high moisture content in the feedstock also lowers the CMF yield due to the dilution of the HCl catalyst.

Zuo et al. (2016) reported the one-pot conversion of carbohydrates to CMF in a deep eutectic solvent (DES) made of $AlCl_3.6H_2O$ and ChoCl using MIBK as the solvent. $AlCl_3.6H_2O$/ChoCl catalyzed the dehydration of fructose into HMF in the DES phase. The HMF got converted into CMF in the MIBK phase by the HCl generated insitu. CMF and HMF were isolated in 50.3% and 8.1% yields, respectively, starting from fructose when the reaction was conducted at 120 °C for 5 h. Under optimized conditions, CMF was obtained in 16.93%, 22.66%, and 17.86% yields from glucose, inulin, and sucrose, respectively.

Le et al. (2017) reported the preparation of BMF from sugars in a DES. A mixture of choline bromide and a metal salt like aluminum sulfate were used as DES. The extracting capability of various organic solvents was examined, and methyl isobutyl ketone was found to be the most efficient one. BMF was obtained in a 50 wt% yield from fructose when the reaction was conducted in a batch reactor at 120 °C for 5 h. A mechanism on the action of deep eutectic solvent for BMF synthesis was also proposed.

Kohl et al. (2017) demonstrated the production of CMF from sugar feedstock in a continuous flow reactor. D-fructose produced CMF in yields up to 74% at 100 °C with a 1:1 ratio of aqueous HCl (37%) and DCE and a residence time of 1 min. On the other hand, sucrose produced CMF in 50% yield after a residence time of 2.5 min. The performance of the continuous flow approach was examined on high fructose corn syrup (HFCS). CMF was isolated in 85% yield at 100 °C using a 1:1.5 ratio of aqueous HCl (37%) and DCE with a residence time of 1.5 min.

Mascal (2019) reviewed the preparation and derivative chemistries of CMF as a biomass-derived chemical building block. The review discussed the straightforward preparation of CMF under mild conditions starting from biomass-derived carbohydrates and untreated cellulosic biomasses. The review critically evaluated the relative advantages and disadvantages of using CMF over HMF for further value addition to fuels and commodity chemicals.

2.2 Literature review of levulinic acid

Substrate	Catalyst	Reaction Conditions	Yield (%)	Reference
Paper sludge	H_2SO_4	210-235 °C, 13-25 s, 1-5% acid then 195-215 °C, 15-30 min, 2-7.5% acid	60	(Fitzpatrick 1997)
Newspaper	10% H_2SO_4	150 °C, 8 h	59.8	(Farone et al. 2000)
Algal biomass	H_2SO_4	160 °C, 43 min	19.5	(Jeong et al. 2010)
Cellulose	2 M H_2SO_4	170 °C, 50 min	34.2	(Szabolcs et al. 2013)
Glucose			40.5	
Fructose			42.7	
Cellulose	$[C_3SO_3Hmim]HSO_4$	170 °C, 5 h	63	(Ren et al. 2015)
Glucose			76.5	
Fructose			93.4	
HMF			56.4	
HMF	2.5 wt% H_2SO_4	150 °C, 20 min	70	(Flannelly et al. 2016)
Fructose		150 °C, 2 h	83	
Furfuryl alcohol	H-ZSM-5-23 (SiO_2/Al_2O_3 molar ratio of 23)	120 °C, 0.5 h, THF-H_2O (4:1)	74	(Mellmer et al. 2015)
Glucose	Ga@mordenite	175 °C, 6 h	59.9	(Kumar et al. 2016)
Starch			46	
Cellulose			49	
Furfuryl alcohol	H-Z (50)	MEK, 20 bar H_2, 140 °C, 23 h	77	(Guzmán et al. 2016)
Glucose	$AlCl_3$/Oxalic acid	155 °C, 1.5 h, 40 wt% ChoCl	51.7	(Bayu et al. 2016)

Cellulose	[BSMim]HSO_4	20% aq. solution, 120 °C, 2 h	39.4	(Shen et al. 2015)
Glucose	0.25 M HCl	120 °C, 4 h	51	(Garcés et al. 2017)
Fructose		130 °C, 3 h	83	
Sugar beet molasses	Amberlyst-36$^{\mathrm{TM}}$	140 °C, 3 h	67	(Kang et al. 2018)
Glucose	Amberlyst-15/Sn-beta	140 °C, 15 h.	42	(Acharjee et al. 2018)
Corn stalk	$FeCl_3$	180 °C, 40 min	48.9	(Zheng et al. 2017)
Glucose	$CrCl_3$+H_3PO_4	170 °C, 4 h	54.2	(Weiqi et al. 2017)
Cellulose	SA-SO_3H	180 °C, 12 h	51.5	(Shen et al. 2017)
Glucose			61.5	

Abbreviations: [C_3SO_3Hmim]HSO_4: 1-methyl-3-(3-sulfopropyl)imidazolium hydrogen sulfate, THF: Tetrahydrofuran, MEK: methyl ethyl ketone, H-Z (50): modified H-ZSM-5 zeolite, [BSMim]HSO_4 : 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate.

Fitzpatrick et al. (1997) described the Biofine$^{\mathrm{TM}}$ process for the commercial-scale preparation of LA from carbohydrate-containing materials. In the first stage of the two-stage process, the carbohydrate content was hydrolyzed using mineral acids like HCl and H_2SO_4 in a pug-flow reactor at 210-235 °C with a short residence of time (13-25 s). The reaction mixture in the first reactor containing furanic intermediates like furfural and HMF was then passed into the second reactor. The second back-mix reactor works at a slightly lower temperature (ca. 195-215 °C) but a longer residence time of 15-30 min where the HMF is rehydrated to LA and formic acid. The process is biomass agnostic and works on any biomass with carbohydrate content, including cellulosic wastes. A slurry of paper sludge obtained from the Kraft process with 42-50% of cellulose content produced nearly 60% of LA.

Farone et al. (2000) patented the synthesis of LA from cellulosic feedstock using mineral acid catalysts like H_2SO_4. A 10% H_2SO_4 catalyzed the one-pot conversion of cellulose (newspaper) to LA at 150 °C with a maximum 59.8% yield of LA after 8 h of reaction. The reaction was optimized on temperature, duration, and concentration of H_2SO_4.

Jeong et al. (2010) proposed a statistical approach for the conversion of marine algal biomass *Gelidium amansii* into LA under the assistance of a homogeneous acid catalyst. In the typical reaction, the authors investigated the H_2SO_4 catalyzed the single-step conversion of marine algal biomass into LA. Up to 19.5% of LA was obtained from *Gelidium amansii* when the reaction was conducted for 43 min at 160 °C. Further, the authors studied the effect of reaction temperature, duration, and catalyst loading on the LA yield.

Szabolcs et al. (2013) reported the microwave-assisted catalytic dehydration of non-edible carbohydrates into LA using H_2SO_4 as a catalyst. LA was obtained in 34.2% yield when cellulose was treated with 2 M H_2SO_4 at 170 °C for 50 min under microwave heating. Under optimized conditions, glucose and fructose produced 40.5 and 42.7% of LA, respectively. The authors also made a comparative study on the preparation of LA under conventional and microwave heating.

Ren et al. (2015) developed various acidic ionic liquids (AILs) for the conversion of cellulose into LA in an autoclave reactor. The authors employed an aqueous solution of AILs for the direct conversion of cellulose into LA. 1-Methyl-3-(3-sulfopropyl)imidazolium hydrogen sulfate ([C_3SO_3Hmim]HSO_4) showed the best catalytic activity with a 63% yield of LA after 5 h at 170 °C. The reaction was optimized on the amount of water, reaction temperature, duration of reaction, and substrate loading. The optimized reaction was extended to other substrates such as glucose, fructose, and HMF, which produced LA in 76.5, 93.4, and 56.4% yield, respectively. The AILs were recycled and reused up to five consecutive cycles.

Flannelly et al. (2016) reported the synthesis of LA from various biomass-derived carbohydrates and HMF using 2.5 wt% H_2SO_4 as the catalyst. HMF and fructose produced LA in 70 and 83% yield at 150 °C after 20 min and 2 h, respectively. The formation of LA and formic acid from HMF and other carbohydrates revealed that LA and formic acid production were not in the stoichiometric ratio.

Mellmer et al. (2015) reported the hydrolysis of furfuryl alcohol to LA under the assistance of heterogeneous Lewis and Brønsted acid catalysts in tetrahydrofuran (THF)-water solvent system. The strong Brønsted acid catalyst H-ZSM-5-23 (SiO_2/Al_2O_3 molar ratio of 23) yielded 74% LA within 0.5 h at 120 °C using the THF-H_2O (4:1) solvent system. The authors studied the influence of reaction temperature, time, and different solvent systems on the conversion of furfural alcohol to LA. The catalyst progressively lost activity due to the formation of humic matter on the surface of the catalyst.

Kumar et al. (2016**)** developed a Gallium-modified mordenite zeolite (Ga@mordenite) solid acid catalyst for the preparation of LA from carbohydrates. The catalyst was prepared by distributing Gallium particles homogeneously over the zeolite surface by the sonochemical method. The catalytic activity of the Ga@mordenite catalyst was examined for the direct conversion of glucose to LA. The presence of both Lewis and Brønsted acid sites in Ga@mordenite effectively catalyzed the conversion of glucose to LA in yields up to 59.9% (175 ℃, 6 h). Studies showed that neither Gallium nor mordenite could catalyze the conversion of glucose to LA. The use of starch and cellulose produced LA in 46 and 49% yield, respectively, under identical conditions. The catalyst was successfully recovered and reused up to four consecutive cycles.

Guzman et al. (2016) reported the solid acid-assisted one-pot production of LA from furfuryl alcohol. Modified H-ZSM-5 zeolite (H-Z (50)) showed the best catalytic activity with a 77% yield of LA within 23 h at 140 ℃ under 20 bar H_2 pressure. The use of methyl ethyl ketone (MEK) as the solvent inhibited the formation of furanic resin. The authors investigated the effect of reaction temperature, time, loading of catalyst, and pressure of H_2 gas.

Bayu et al. (2016) reported the conversion of glucose to LA using metal chlorides like $ZnCl_2$, CuCl, $AlCl_3$, and $SnCl_2$ in aqueous choline chloride (ChoCl). Among all the investigated metal chlorides, $AlCl_3$ showed the best activity by promoting the isomerization of glucose to fructose and produced LA in 38% yield. Interestingly, the combination of Lewis and Brønsted acid catalysts such as $AlCl_3$ and oxalic acid produced LA in 51.7 % yield under identical reaction conditions (155 °C, 1.5 h). The addition of oxalic acid facilitates the rehydration of HMF into LA, whereas choline chloride slows down the rehydration of HMF. The catalyst could be recycled and reused up to three consecutive cycles without significant loss in their catalytic activity.

Shen et al. (2016) produced LA from cellulose using SO_3H-functionalized ionic liquids (ILs) as an acid catalyst. Three different ILs, namely, [BSMim]HSO_4, [BSMim]OAc, and [BSMim]CF_3SO_3 were used. Among them, 20% aqueous solution of [BSMim]HSO_4 (1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate) produced LA in 39.4% yield within 2 h at 120 °C. The proposed H_2O-[BSMim]HSO_4 catalyst played the role of both solvent and acid catalyst. The H_2O-[BSMim]HSO_4 catalyst was recycled and reused up to four times without significant loss in catalytic activity.

Garces et al. (2017) investigated the HCl-catalyzed dehydration of glucose and fructose in aqueous media using a batch autoclave reactor. The study revealed that reaction temperature and HCl concentration are crucial parameters for converting glucose into LA. A maximum of 51% yield of LA was achieved from glucose when the reaction was conducted for 4 h at 120 °C using 0.25 M HCl. Further increase in the reaction temperature and acid concentration led to more humic matter formation. LA was obtained in 83% yield starting from fructose (130 °C, 3 h, 0.25 M HCl).

Kang et al. (2018) reported the conversion of pretreated sugar beet molasses (IE) to LA using Amberlyst-36 as a heterogeneous catalyst. Up to 67% yield of LA was achieved from IE within 3 h at 140 °C. The untreated sugar beet molasses deactivated the catalytic activity by forming a solid resin on the surface of the Amberlyst-36 catalyst.

Acharjee et al. (2018) investigated the effect of Brønsted-Lewis dual solid acid catalyst for the conversion of glucose to LA in a batch reactor. Among the catalysts studied, Amberlyst-15/Sn-beta afforded LA in 42% yield after 15 h at 140 °C. The authors investigated the role of Amberlyst-15 and Sn-beta catalysts, individually, for the conversion of glucose to LA. They found that the strong Brønsted acidity of Amberlyst-15 failed to catalyze the isomerization of glucose to fructose. Therefore, only 37% yield of LA was obtained from glucose after 24 h at 140 °C. On the other hand, the Sn-beta catalyst effectively catalyzed the isomerization of glucose to fructose but failed to produce LA in high yield. However, the catalysts got deactivated during the reaction due to the deposition of humin on the surface.

Zheng et al. (2017) reported the $FeCl_3$-assisted one-pot preparation of LA from corn stalk. In a closed batch reactor, $FeCl_3$ catalyzes the conversion of corn stalk to LA in 49% yield within 40 min at 180 °C. The reaction was optimized on the reaction temperature, duration of reaction, and the loading of $FeCl_3$. In addition, the authors developed a broadly applicable kinetic model to interpret corn stalk conversion into glucose, HMF, and LA.

Weiqi et al. (2017) reported various homogeneous Brønsted and Lewis acid-catalyzed synthesis of LA from glucose in a batch reactor. The authors the combination of mineral acids and metal chlorides for the conversion of glucose into LA. Among the examined catalysts, $CrCl_3$ showed excellent catalytic activity where the quantitative conversion of glucose was achieved after 4 h at 170 °C, and LA was obtained in 23.56% yield. Under the optimized conditions, the combination of $CrCl_3$ and H_3PO_4 ($CrCl_3$+H_3PO_4) produced 54.24% of LA from glucose, which is significantly higher than $CrCl_3$ or H_3PO_4 alone.

Shen et al. (2018) prepared a cellulase-mimetic solid acid catalyst for the conversion of cellulose into LA in water. A sulfonic acid-functionalized sucralose-based catalyst SA-SO_3H and sucrose-based SO-SO_3H (silica/carbon porous composite bearing −Cl and −SO_3H binding site) were prepared for the conversion of cellulose into LA. Among the examined catalysts, SA-SO_3H produced a maximum of 51.5% of LA from cellulose after 12 h at 180 °C. The higher catalytic activity of SA-SO_3H over SO-SO_3H was mainly due to the presence of -Cl groups in the active sites. Interestingly, under the same set of reaction conditions, glucose produced LA in 61.5% yield. Finally, the catalyst reusability studies revealed that the catalyst progressively loses its catalytic activity due to the leaching of binding sites and the adsorption of humins on the catalyst surface.

2.3 Literature review of 5-(alkoxymethyl)furfurals (AMF)

Substrate	Reaction Conditions	Product	Yield (%)	Reference
HMF	Z-SBA-15, 140 °C, 5 h, EtOH	EMF	76	(Lanzafame et al. 2011)
	SZ-SBA-15, 140 °C, 5 h, EtOH		62	
	Al-MCM-41(25), 140 °C, 5 h, EtOH		37	
	Al-MCM-41(50), 140 °C, 5 h, EtOH		68	
HMF	H_2SO_4, 75 °C, 24 h, EtOH	EMF	81	(Balakrishnan et al. 2012)
	H_2SO_4, 75 °C, 24 h, BuOH	BuMF	76	
	Dowex DR2030, 75 °C, 24 h, EtOH	EMF	57	
	Amberlyst-15, 75 °C, 24 h, EtOH		55	
	Dowex 50WX8, 75 °C, 24 h, EtOH		45	
	Amberlite IR120, 75 °C, 24 h, EtOH		33	
Fructose	H_2SO_4, 100 °C, 24 h	EMF	70	
	Amberlyst-15, 100 °C, 24 h		71	
	Silica sulphuric acid, 100 °C, 24 h		69	
	Dowex DR2030, 100 °C, 24 h		68	
	Dowex 50WX8, 100 °C, 24 h		56	
Glucose	Sn-BEA/Amberlyst 131, 90 °C, 13 h, EtOH	EMF	31	(Lew et al. 2012)
Fructose	Sn-BEA/Amberlyst 131, 70 °C, 12 h, EtOH		93	
HMF	Sn-BEA/Amberlyst 131, 70 °C, 12 h, EtOH		100	
Glucose	$AlCl_3.6H_2O$, 160 °C, 15 min, EtOH	EMF	33	(Yang et al. 2012)
HMF			70	

Fructose			46	
Fructose	MSIC, 100 °C, 20 min, EtOH	EMF	57	(Kraus et al. 2012)
	MSIC, 100 °C, 20 min, MeOH	MMF	54	
HMF	$H_3PW_{12}O_{40}$, 70 °C, 24 h, EtOH	EMF	85.3	(Bing et al. 2012)
	$[MIMBS]_3PW_{12}O_{40}$, 70 °C, 24 h, EtOH		90.7	
HMF	$Fe_3O_4@SiO_2$-PTA, 100 °C, 24 h, EtOH	EMF	83.6	(Wang et al. 2013)
Fructose	$Fe_3O_4@SiO_2$-PTA, 100 °C, 24 h, EtOH		55	
HMF	GO, 100 °C, 12 h, EtOH	EMF	92	(Wang et al. 2013)
Fructose	DMSO-ethanol, 130 °C, 24 h	EMF	71	
Sucrose			34	
Inulin			66	
Fructose	$AlCl_3$, 100 °C, 11 h, EtOH	EMF	71	(Liu et al. 2013)
Glucose			38	
HMF			92.9	
HMF	$Fe_3O_4@SiO_2$-SO_3H, 100 °C, 10 h, EtOH	EMF	89.3	(Zhang et al. 2014)
Fructose	$Fe_3O_4@SiO_2$-SO_3H, 100 °C, 15 h, EtOH		72.3	
Sucrose			40.2	
Inulin			63.3	
HMF	K-10 clay-HPW, 100 °C, 10 h, EtOH	EMF	92	(Liu et al. 2014)
Fructose			66	
Fructose	Lys/PW (2), 120 °C, 15 h EtOH/DMSO	EMF	76.6	(Li et al. 2014)
Inulin			58.5	
Sorbose			42.4	
Sucrose			36.5	
Fructose	DMSO/H_2SO_4, 140 °C, 8 h	EMF	55	(Liu et al. 2015)
Glucose	DMSO/H_2SO_4, $SnCl_4$, 140 °C, 8 h	EMF	15	
Inulin			51	

Agar			16	
Sucrose			22	
Cellobiose			8	
Fructose	Ar-SO_3H-SBA-15, 116 °C, 4 h, EtOH/DMSO	EMF	63.4	(Morales et al. 2017)
Glucose	PTSA–POM/$AlCl_3.6H_2O$, 150 °C, 30 min, EtOH/H_2O	EMF	30.6	(Xin et al. 2017)
Fructose	D0.5-SPC-0.25-9/3, 140 °C, EtOH/THF	EMF	68	(Dai et al. 2019)
Fructose	PTA/SBA-15, EtOH, 100 °C, 24 h	EMF	67	(Patil et al. 2018)
Glucose	MFI–Sn/Al (100/100), EtOH, 140 °C, 9 h	EMF	44	(Bai et al. 2018)
Corn stover	H_2SO_4/USY, EtOH, 210 °C, 125 min	EMF	23.9	(Chen et al. 2019)

Abbreviations: Z-SBA-15 (zirconia over SBA-15), SZ-SBA-15 (Sulfated Zirconia-SBA-15), Al-MCM-41(Al-containing mesoporous silica sample with different Si/Al ratio), MSIC (1-methyl-3-(3-sulfopropyl)-imidazolium chloride), $[MIMBS]_3PW_{12}O_{40}$ (phosphotungstic acid /methylimidazolebutylsulfate), GO (Graphene oxide), Lys/PW (lysine/ phosphotungstic acid), Ar-SO_3H-SBA-15 (Arenesulfonic acid-modified SBA-15 mesostructured silica), PTSA-POM (p-formaldehyde supported on p-tolounesulphonic acid), D0.5-SPC-0.25-9/3 (double-hydrogen-bonded sulfonated polymer catalyst), MFI–Sn/Al (hierarchical lamellar multifunctional Meso-/microporos zeolite catalyst),

Lanzafame et al. (2011) studied the etherification of HMF in ethanol using mesoporous silica catalysts at 140 °C for 5 h in a Parr autoclave reactor. Among the various acid catalysts examined, zirconia over SBA-15 (Z-SBA-15) showed the best activity with 76% yield of EMF. Interestingly, the sulfated zirconia-SBA-15 (SZ-SBA-15) yielded only 62% of EMF due to the decreased Lewis acidity. These results reveal that Lewis acidity favors EMF production, whereas the Brønsted acid catalysts favor the ring-opening of HMF into EL. The etherification of HMF was then examined over MCM-

41 catalysts such as Al-MCM-41 (with different Si/Al ratio). Al-MCM-41 (25) and Al-MCM-41 (50) accounted for 37% and 68% yield of EMF, respectively. The results were explained by more Lewis acidic sites due to increased aluminum content in the catalysts. However, the Al-MCM-41 (75) catalyst failed to produce EMF due to Brønsted acidic sites on the surface.

Balakrishnan et al. (2012) examined the effect of homogeneous and heterogeneous catalysts on the etherification of HMF into EMF. The reactions were conducted at 75 °C for 24 h in a sealed vessel. In the presence of H_2SO_4 (5 mol%) as a homogeneous catalyst, EMF and BuMF were obtained in 81 and 76% yields, respectively. Among the heterogeneous solid acid catalysts examined, Dowex DR2030 was found to be most effective with an EMF yield of 57%. Amberlyst-15, Dowex 50WX8, and Amberlite IR120 provided EMF yields in 55, 45, and 33%, respectively. The authors also attempted a one-pot production of EMF starting from fructose. An H_2SO_4-catalyzed dehydration/etherification of fructose in ethanol (100 °C, 24 h) gave EMF in 70% yield. Among the heterogeneous catalysts, Amberlyst-15 worked best with 71% yield of EMF. Under identical conditions, silica sulphuric acid, Dowex DR2030, and Dowex 50WX8 provided 69, 68, and 56% yield of EMF, respectively.

Lew et al. (2012) reported a one-pot synthesis of EMF by the ethanolysis of glucose using a combination of Sn-BEA and Amberlyst 131 catalyst. The reaction proceeds by the isomerization of glucose to fructose, followed by dehydration of fructose, and finally etherification of the HMF intermediate. The role of individual catalysts on EMF yield was also analyzed. When the reaction was conducted at 90 °C for 5 h using the Sn-BEA alone, the isomerization of glucose into fructose was only observed. Therefore, Sn-BEA could not catalyze the dehydration of fructose into HMF. However, ethanolysis of glucose by Amberlyst 131 catalyst (90 °C, 8 h) successfully produced EMF, although in lower (ca. 31%) yield. Furthermore, the influence of the Amberlyst 131 catalyst was examined on fructose and HMF, which produced EMF in 93% and 100% yield, respectively, when the reaction was conducted 70 °C for 12 h.

Yang et al. (2012) reported the conversion of glucose into furanics using $AlCl_3$ in aqueous ethanol under microwave irradiation. Although the total yield of furanics (e.g., HMF, EMF, and EL) was as high as 57%, the yield of EMF was poor (ca. 33%). The reaction parameters like temperature, catalyst loading, and ethanol/water ratio were optimized. A significant amount of ethyl glucoside (EGL) (ca. 19%) and humin formed when anhydrous ethanol was used as a reaction medium. EGL is an intermediate in the glucose-to-EMF transformation. Increasing the water content, use of $AlCl_3.6H_2O$, and increasing the reaction temperature help facilitate the reversal of EGL to glucose, thereby increasing the EMF yield. The optimal conditions were 10 wt% water in ethanol, 160 °C, 15 min of reaction time, and 0.4 mmol of $AlCl_3.6H_2O$ catalyst. Under the optimized conditions, HMF and fructose produced 70 and 46% of EMF, respectively.

Kraus et al. (2012) reported the production of AMFs from fructose using imidazolium sulfonic acid ionic liquids. When fructose, 1-methyl-3-(3-sulfopropyl)-imidazolium chloride (MSIC), methanol and hexanes were placed in a sealed tube and heated at 100 °C for 20 min, MMF was produced in 57% yield. The use of ethanol as the solvent under identical conditions produced EMF in 54% yield.

Bing et al. (2012) developed a solid organic-inorganic hybrid catalyst $[MIMBS]_3PW_{12}O_{40}$ for the etherification of HMF in ethanol at 70 °C for 24 h. Initially, the etherification reaction of HMF in ethanol was carried out using phosphotungstic acid ($H_3PW_{12}O_{40}$) and methylimidazolebutylsulfate (MIMBS) separately. Only 85.3% EMF was obtained with $H_3PW_{12}O_{40}$ catalyzed reaction, whereas MIMBS failed to catalyze the reaction. However, the hybrid catalyst $[MIMBS]_3PW_{12}O_{40}$ showed better catalytic activity with an EMF yield reaching as high as 90.7%. The catalyst was then applied to the one-pot dehydrative etherification of fructose into EMF under identical conditions. Only 15.4% of EMF was obtained due to the slow dehydration of fructose at 70 °C. Increasing the temperature to 90 °C, 90.5% of EMF was achieved from fructose using only 5 mol% of the catalyst. Interestingly, $[MIMBS]_3PW_{12}O_{40}$ catalyst could not promote the isomerization of glucose to fructose. Hence no EMF was produced from glucose and cellulosic biomass. The catalyst was successfully recovered and reused several times without significant loss in catalytic activity.

Wang et al. (2013) developed $Fe_3O_4@SiO_2$ magnetic nanoparticles (MNP) supported on phosphotungstic acid (PTA) for the synthesis of EMF from HMF and fructose. The synthesized $Fe_3O_4@SiO_2$-PTA catalyst was confirmed by XRD, TEM, and FTIR techniques. Further, the content of tungsten (W) in the supported framework was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES), and its surface acidity was determined by potentiometric titration with n-butylamine. In a typical reaction, HMF, Fe_3O_4@SiO_2-PTA, and ethanol were refluxed under a nitrogen atmosphere for 24 h to produce EMF in an 83.6% yield. In addition, the Fe_3O_4@SiO_2-PTA catalyst produced EMF in 55% yield directly from fructose The Fe_3O_4@SiO_2-PTA catalyst can effectively be recovered from the reaction mixture using an external magnetic field and reused for five times without loss of catalytic activity.

Wang et al. (2013) reported a one-pot conversion of sugars to EMF using the Graphene oxide (GO) catalyst. Specifically, the one-pot conversion of fructose, sucrose, and inulin in DMSO-ethanol at 130 °C for 24 h gave EMF in 71%, 34%, and 66% yield, respectively. In addition, the etherification of HMF in ethanol gave EMF in 92% yield when the reaction was conducted at 100 °C for 12 h using GO catalyst. The reaction temperature and catalyst loading were optimized for the best selectivity and yield of EMF. The GO catalyst was successfully recycled and reused.

Liu et al. (2013) reported a one-pot synthesis of EMF by ethanolysis of biomass-derived carbohydrates using the $AlCl_3$ catalyst. The authors observed that the increase in reaction temperature (>100 °C) lowers the selectivity towards EMF by forming more EL and humic matter. The reaction completed after 11 h at 100 °C using 10 mol% of the catalyst. Under optimized conditions, fructose and glucose provided 71 and 38% of EMF, respectively. Further, the authors converted HMF into EMF in 92.9% yield.

Zhang et al. (2014) reported the synthesis of magnetically-recoverable Fe_3O_4@SiO_2-SO_3H catalyst by immobilizing sulfonic acid over the surface of silica-encapsulated Fe_3O_4 nanoparticles for the preparation of EMF from HMF in high yield (ca. 89.3%). EMF formed in 72.3% yield by the direct one-pot dehydrative etherification of fructose at 100 °C for 15 h with 200 mg of the catalyst. Efficiency of the Fe_3O_4@SiO_2-SO_3H catalyst was examined on fructose-based carbohydrates, a high EMF yield 40.2% and 63.3% was obtained from sucrose and inulin, respectively. The lower yield of EMF from sucrose was due to slower isomerization of the glucose unit into fructose. The catalyst was recovered by using an external magnet and reused several times without a significant loss in catalytic activity.

Liu et al. (2014) developed a HPW catalyst supported on montmorillonite K10 for the one-pot synthesis of EMF from HMF and fructose. The solid acid catalyst was conveniently synthesized by the immobilization of HPW on K10. The yield of EMF improved by increasing the HPW loading from 10-30 wt% with the yield reaching as high as 92% when the reaction was conducted at 100 °C for 10 h. In addition, a one-pot synthesis of EMF was achieved in 66% yield starting from fructose. The catalyst was recovered and reused several times without the significant loss of its catalytic activity.

Li et al. (2015) developed a series of heterogeneous acid-base bifunctional hybrid nanospheres prepared from basic amino acids with phosphotungstic acid (HPA) with specific molar ratios. Among the series of nanocatalysts examined, Lys/PW (2) (1:2 molar ratios of lysine to HPA) produced EMF in 76.6% yield from fructose at 120 °C and 15 h of reaction time. The reaction was optimized on the reaction temperature, duration, type, and loading of catalyst. EMF was obtained in 58.5%, 42.4%, and 36.5% yield from inulin, sorbose, and sucrose, respectively. The catalyst was successfully recovered and reused several times.

Liu et al. (2015) reported a novel and environmentally friendly process for the conversion of carbohydrates to EMF under the assistance of the DMSO/H_2SO_4 catalyst. The preparation of EMF from fructose in ethanol was examined over various homogeneous acid catalysts. Among them, 5 mmol of the DMSO/H_2SO_4 catalyst produced EMF in 55% yield after 8 h at 140 °C. The optimized conditions were then extended for the conversion of other carbohydrates to EMF in ethanol medium. Inulin, agar, sucrose, and cellobiose produced EMF in 51, 16, 22, and 8% of EMF, respectively.

Morales et al. (2016) investigated the direct conversion of fructose to EMF using arylsulfonic acid-modified SBA-15 mesostructured silica (Ar-SO_3H-SBA-15) catalyst in the ethanol/DMSO mixture. The kinetic study of the reaction revealed that DMSO stabilized the furanose form of the fructose and limits the rehydration of HMF into LA and humin. The yield of EMF from fructose reached 63.4% at 116 °C for 4 h in ethanol in the presence of 8.3 vol.% of DMSO and 13.5 mol% of Ar-SO_3H-SBA-15 catalyst. The catalytic efficiency declined gradually due to the formation of organic deposits on the surface of the catalyst.

Xin et al. (2017) investigated the dehydration of glucose to HMF and EMF under the assistance of both Lewis and Brønsted acid catalyst. Initial efforts were made to synthesize HMF by direct one-pot dehydration of glucose in GVL/H_2O (10:1) system in the presence of PTSA-POM/$AlCl_3.6H_2O$ catalyst. HMF was obtained in 60.7% yield within 60 min at 140 °C. The authors examined the role of PTSA-POM and $AlCl_3.6H_2O$ on HMF yield. They found that $AlCl_3.6H_2O$ effectively catalyzes the isomerization of glucose to fructose in GVL/H_2O system. In order to explore the catalytic efficiency, the authors extended the process for the direct synthesis of EMF form glucose in ethanol/H_2O system (9:1) at 150 °C for 30 min. The catalyst PTSA-POM/$AlCl_3.6H_2O$ effectively catalyzed the direct dehydrative etherification of glucose with a combined yield of 42.1% of EMF and HMF.

Patil et al. (2018) reported that PTA supported on SBA-15 (PTA-SBA-15) can be used as a catalyst with tunable acidity for the direct conversion of fructose to HMF and EMF in ethanol medium at 100 °C. This composite gave the highest yield of EMF (67%) at a lower catalyst loading compared to the literature reports. Moreover, this is the first report on the use of PTA/SBA-15 composites, which afforded nearly quantitative conversion of fructose with a 67% yield of EMF. The catalysts can be recycled and reuse up to three cycles without any appreciable change in EMF yield.

Bai et al. (2018) designed and developed a hierarchical lamellar multifunctional MFI–Sn/Al meso-/microporos zeolite catalyst for the synthesis EMF from glucose via a three-step reaction cascade. The co-existence of both Lewis acidic (Sn) sites and the Brønsted acidic (Al–O(H)–Si) sites with meso-/microporosity of the MFI–Sn/Al catalyst effectively catalyzed the synthesis of EMF from carbohydrates. A series of MFI–Sn/Al catalysts were synthesized by varying the Lewis and Brønsted acidic sites. Among all the examined MFI–Sn/Al catalysts, MFI–Sn/Al (100/100) showed the best catalytic activity with 44% EMF yield from glucose in ethanol after 9 h at 140 °C.

Dai et al. (2019) reported a double-hydrogen-bonded sulfonated polymer catalyst (D-SPC) with tunable acidity as a novel solid organocatalyst for the direct one-pot production of EMF from fructose at 140 °C in ethanol/THF (3:1) Solvent system. The authors synthesized the SPC catalyst by the oxidative copolymerization of Aniline and 2,2′-benzidinedisulfonic acid in water using ammonium persulfate as oxidant. The acidic strength of the catalyst has inverse relation with the EMF yield. The catalyst with weaker acidic strength but suitable acid density (ca. 2.5 mmol g^{-1}) was found to favor the one-pot preparation of EMF.

Chen et al. (2019) described a mixed acid catalyst (0.1% H_2SO_4 and 1.0% zeolite USY) assisted the one-pot production of EMF from corn stover in ethanol. The reactions were conducted in a stainless steel reactor at 210 °C, and EMF was isolated in a 23.9% yield after 125 min. Then kinetic studies of the reaction showed that EMF production from corn stover follows first-order kinetics. Furthermore, the effect of reaction temperature, duration, and catalyst loading on EMF production was investigated. The catalyst was recovered and reused for five consecutive cycles.

2.4 Literature review of alkyl levulinates (ALs)

Substrate	Reaction Conditions	Product	Yield (%)	Reference
LA	DPTA/K10, BuOH, 120 °C, 4 h	BL	97	(Dharne et al. 2011)
LA	40WD-S, EtOH, 78 °C, 10 h	EL	76	(Pasquale et al. 2012)
Cellulose	H_2SO_4, MeOH, 210 °C, 2 h	ML	50	(Li et al. 2013)
LA	DPTA/H-ZSM-5_{97}, EtOH, 78 °C, 4 h	EL	93	(Nandiwale et al. 2013)
Fructose	IL-PTA, EtOH, 120 °C, 12 h	EL	80	(Chen et al. 2014)
Inulin			67	
Sucrose			45	
Glucose			7	
LA	S-ZrSBA15(10.7), EtOH, 70 °C, 24 h	EL	79	(Kuwahara et al. 2014)
Glucose	S-ZrSBA15(10.7), MeOH, 200 °C, 3 h	ML	4.7	
Fructose			33.3	
LA	UiO-66-NH_2, EtOH, 78 °C, 8 h	EL	95	(Cirujano et al. 2015)

α-Angelica lactone	Amberlyst-36, BuOH, 75 °C, 4 h	BL	94	(Al-Shaal et al. 2015)
LA			56	
Fructose	PTA/H-ZSM-5, EtOH, 160 °C, 2 h	EL	40.6	(Zhao et al. 2015)
Cellulose			8.7	
Glucose			19	
Sucrose			27.3	
Inulin			37.4	
LA	12.2% PTA/ZrO_2-Si(Et)-Si-NTs-1.0, EtOH, 65 °C, 1 h	EL	74.8	(Song et al. 2016)
	12.2% PTA/ZrO_2–Si(Et)-Si-NTs-1.0, BuOH, 65 °C, 1 h	BL	69.6	
α-Angelica lactone	$Ch_1H_5P_2W_{18}O_{62}$, BuOH, 75 °C, 1 h	BL	84	(Yi et al. 2017)
HMF	[Cu-BTC][PMA], EtOH, 140 °C, 14 h	EL	20.2	(Wang et al. 2016)
LA	Amberlyst-15, MeOH, 65 °C, 6 h	ML	82	(Ramli et al. 2017)
Cellulose	5-Cl-SHPAO, EtOH, 160 °C, 4 h	EL	60	(Yu et al. 2017)
Glucose			61	
Fructose			68	
Sucrose			62	
LA	GC400, BuOH, 100 °C, 4 h	BL	90.5	(Yang et al. 2018)
Cellulose	$Al_2(SO_4)_3$, MeOH, 180 °C, 40 min	ML	70.6	(Huang et al. 2018)
Glucose	$H_2Zr_1PW_{12}O_{40}$+Sn-Beta, EtOH, 180 °C, 3 h	EL	54	(Mulik et al. 2019)
Glucose	AlPTA, MeOH, 160 °C, 0.5 h	ML	64.4	(Zhang et al. 2019)
Fructose			69.8	
Sucrose			65.2	

Cellulose			45.2	
LA	0.08% SO_3H-Bz-Al-SBA-15, EtOH, 80 °C, 2 h	EL	94	(Kumaravel et al. 2019)
LA	C-SO_3H, EtOH, 120 °C, 9 h	EL	88.2	(Liu et al. 2019)

Abbreviations: DPTA/K10: dodecamolybdophosphoric acid support on K10 clay, IL-PTA: ($[3.2H]_3[PW_{12}O_{40}]_2$),
S-ZrSBA15(10.7) (mesoporous sulfated zirconosilicates with Si/Zr atomic ratio is 10.7), 12.2% PTA/ZrO_2–Si(Et)-Si-NTs-1.0 (x= 12.2 wt% of PTA and y=1.0 molar ratio of Zr/Si), 5-Cl-SHPAO: chlorinated sulfonated hyperbranched poly (arylene oxindole), GC400: glucose-derived amorphous carbon, AlPTA: aluminum phosphotungstate

Dharne et al. (2011) reported the esterification of LA using dodecamolybdophosphoric acid (DPTA) supported on montmorillonite clay (K10) as the catalyst. The catalytic activity of the synthesized catalysts was in the following order DPTA-K10>DMAA-K10>STH-K10>K10. The yield of BL increased incrementally with an increase in the loading of DPTA from 10 to 30 wt%. Under optimized conditions, the 20 wt% DPTA-K10 catalyst produced BL in 97% yield within 4 h at 120 °C using butanol to LA molar ratio of 6:1.

Pasquale et al. (2012) developed a heterogeneous catalyst for the esterification of LA under mild conditions. The catalyst was prepared by incorporating Wells-Dawson HPA in the silica framework by using the sol-gel technique. The 20WD-S (2.7 g of WD in 14.7 g of pure silica) and 40WD-S (5.0 g of WD in 14.7 g of pure silica) catalysts were prepared by varying the amount of WD acid. The preparation of EL was attempted from LA in a batch reactor (78 °C, 10 h). A 76% yield of EL was obtained with 40WD-S as the catalyst, whereas 20WD-S produced significantly less EL. Further, a comparative study between the homogeneous Keggin and WD-type HPA and their silica-supported heterogeneous counterparts was carried out focusing on the yield of EL. Commercial Keggin and WD-type HPA provided EL in 92 and 93% yield, respectively. Even though the heterogeneous 40WD-Si catalyst gave a lower yield of EL than the homogeneous catalysts, the recovery of the catalyst was straightforward. The catalyst was recovered and reused up to the fourth catalytic cycle with little loss, but the catalyst leached out from supporting material in the following cycles.

Li et al. (2013) investigated the one-pot preparation of methyl levulinate (ML) from cellulose. The methanolysis of cellulose was carried out for 2 h at 210 °C using sulfuric acid as the catalyst. A high yield of around 50% of ML was achieved with a sulfuric acid concentration of 0.01 mol/L and initial cellulose concentration below 100g/L.

Nandiwale et al. (2013) supported dodecaphosphotungstic acid on desilicated H-ZSM-5 (PTA/DH-ZSM-5) and used them as catalysts for the preparation of EL from LA. The catalysts were named based on the crystallinity, such as H-ZSM-5_{100} (fully crystalline), H-ZSM-5_{97}, H-ZSM-5_{72}, and H-ZSM-5_{65}. Among the examined catalysts, 15 wt% DPTA/H-ZSM-5_{97} catalyst gave 93% EL within 4 h at 78 °C. Reaction parameters such as temperature, duration, catalyst to LA ratio, and LA to ethanol molar ratio were optimized. The catalyst was recovered and reused up to the fourth cycle.

Chen et al. (2014) reported a direct conversion of fructose to EL using ionic liquid-based polyoxometalates (IL-POM). The IL-PTA showed the best catalytic activity and produced EL in an 80% yield within 12 h at 120 °C. Under similar conditions, IL-STA and IL-PMA produced EL in 72 and 47% yield, respectively, starting from fructose. The observed difference in yield may be correlated with their relative acidic strength. On the other hand, the use of commercial PTA as a homogeneous catalyst produced EL in 84% yield. Although a high EL yield was achieved, the separation of homogenous catalysts from the reaction mixture was challenging. In this aspect, the heterogeneous IL-POMs were preferred over the homogeneous catalysts. Under the optimized conditions, inulin and sucrose produced 67 and 45% of EL, respectively. Glucose gave only 7% EL even after 24 h at 120 °C.

Kuwahara et al. (2014) reported the esterification of LA with ethanol using sulfated zirconosilicates as a solid acid catalyst. Two types of mesoporous sulfated zirconosilicates catalysts were prepared using different zirconium sources. The S-ZrSBA15 catalyst was prepared using $ZrOCl_2 \cdot 8H_2O$ under neutral condition, whereas the S-mesoZS was prepared using $Zr(O^nPr)_4$ in strong acid. Among the examined catalysts, S-ZrSBA15 was found to be the most effective catalyst, affording 79.0% yield of EL after 24 h of reaction at 70 °C. Then the catalytic efficiency of S-ZrSBA15(10.7) was examined on the direct dehydrative etherification of glucose and fructose in methanol at 200 °C for 3 h produce ML in 4.7% and 33.3% yield, respectively.

Cirujano et al. (2015) developed a stable heterogeneous Zr-containing metal-organic frameworks (Zr-MOFs) for the esterification of LA. The authors prepared heterogeneous Zr-MOFs from terephthalate (UiO-66) or 2-aminoterephthalate ligands (UiO-66–NH_2). The catalytic performance of synthesized Zr-MOFs was examined on the esterification of LA in ethanol. A 95% yield of EL was obtained after 8 h at 78 °C using UiO-66-NH_2 as the ligand. Further, the authors made a detailed investigation on the alcohol chain length, particle size, functional group substitution at the ligand benzene ring, and contents of defects on the catalytic activity of the MOFs. Interestingly, UiO-66–NH_2, exhibited the dual acid-base activation mechanism to activate LA at the Zr sites and the alcohol at the amino groups of the ligand. The catalyst was recycled and reused up to three consecutive cycles without significant loss of activity.

Al-Shaal et al. (2015) reported the preparation of levulinate esters from α-angelica lactone using Amberlyst-36 catalyst. A 94% yield of BL was obtained when the reaction was conducted in butanol for 4 h at 75 °C. Further, the authors optimized the reaction parameters like temperature, duration of reaction, and the loading of catalyst on the yield of BL. The optimized reaction conditions were then applied for the synthesis of other ALs from α-angelica lactone using different alkyl alcohols.

Zhao et al. (2015) prepared a series of various supported PTA catalysts such as PTA/β, PTA/Snβ, PTA/H-Y, PTA/H-ZSM-5, PTA/USY, PTA/ReUSY, and PTA/SBA-15 for the one-pot synthesis of EL from carbohydrates. Among the examined catalysts, 20 wt% PTA/H-ZSM-5 provided 40.6 % EL yield from fructose after 2 h at 160 °C, whereas the PTA/Sn β and PTA/β provided EL in 24% and 7% yield, respectively. Although the unsupported catalyst provided a slightly higher yield of EL (49.6%) from fructose, the recovery of the catalyst was not efficient. The catalyst was successfully recovered and reused the catalyst for up to four consecutive cycles.

Song et al. (2016) developed a novel PTA supported on zirconia-functionalized organosilica nanotube as a solid acid catalyst. They prepared series of x% PTA/ZrO_2-Si(Et)-Si-NTs-y catalyst (x=10.4-12.2 wt% of PTA and y=0.5-1.0 molar ratio of Zr/Si) by varying PTA concentration and Zr/Si molar ratio for the esterification of LA. Among the catalysts examined, 12.2% PTA/ZrO_2-Si(Et)-Si-NTs-1.0 (x=12.2 wt% of PTA and y=1.0 molar ratio of Zr/Si) effectively catalyzed the esterification of LA in ethanol and butanol at 65 °C with 74.8 and 69.6% yield of EL and BL, respectively. Further, the catalyst could be recycled and reused up to three catalytic cycles without significant loss of their activity.

Yi et al. (2016) developed a series of choline chloride (ChoCl)-exchanged HPA catalyst $Ch_xH_{(6-X)}P_2W_{18}O_{62}$ (x=1-6) for the synthesis of BL from α-angelica lactone. The $Ch_1H_5P_2W_{18}O_{62}$ catalyst effectively produced BL in 84% yield after 1 h at 75 °C. The control reaction with choline chloride alone showed only 5% and 13% conversion of α-angelica lactone, respectively. Interestingly, the commercial $H_6P_2W_{18}O_{62}$ catalyst produced 95.1% BL under identical conditions. However, homogeneous nature of the catalyst complicated the isolation, purification, and recovery of the catalyst. In this regard, ChoCl-exchanged HPA catalysts were preferred, albeit of lower BL yield. The $Ch_1H_5P_2W_{18}O_{62}$, $Ch_2H_4P_2W_{18}O_{62}$, $Ch_3H_4P_2W_{18}O_{62}$, $Ch_4H_4P_2W_{18}O_{62}$, $Ch_5HP_2W_{18}O_{62}$, and $Ch_6P_2W_{18}O_{62}$ catalysts produced BL in 84, 79.4, 38.2, 21.5, 9.9, and 9.2% of BL, respectively. This observation was correlated with a decrease in acidity from $Ch_1H_5P_2W_{18}O_{62}$ to $Ch_6P_2W_{18}O_{62}$ catalyst.

Wang et al. (2016) developed a Cu-based metal-organic framework (MOF) supported polyoxometalate catalyst (POM-MOF) for the synthesis of EL from HMF. The PMA catalyst was supported on a Cu-based MOF, and the resulting [Cu-BTC][PMA] was employed for the preparation of EL from HMF. The catalytic efficiency of the synthesized catalyst was compared with Cu-BTC and PMA alone. Both PMA and [Cu-BTC][PMA] produced EL, albeit of low yields (<10%). However, Cu-BTC alone failed to catalyze the reaction. The parametric studies showed that increasing the reaction temperature from 80 to 140 °C improved the yield of EL from 3 to 20.2%. Interestingly, [Zn-BTC] [PMA] and [Co-BTC][PMA] catalysts did not produce any EL from HMF.

Ramli et al. (2016) reported the synthesis of ALs from LA using Amberlyst-15 as a solid acid catalyst. Nearly 82% of ML was achieved with 30 wt% Amberlyst-15 loading using a 1:20 molar ratio of LA and methanol at a temperature of 65 °C and a duration of 6 h. The optimized conditions were then extended to the synthesis of other ALs. The Amberlyst-15 catalyst was conveniently recovered and reused up to five cycles.

Yu et al. (2017) developed a sulfonated hyperbranched poly(arylene oxindole) (SHPAOs) catalyst for the direct conversion of carbohydrates into levulinates. The chlorinated SHPAO (5-Cl-SHPAO) exhibited the best catalytic efficiency with a 60% yield of EL from cellulose within 4 h at 160 ℃. The optimized reaction was then extended to the alcoholysis of cellulose in other monohydric alcohols. ML was obtained in only 25% yield, whereas PL and BL were obtained in 60 and 62% yield, respectively. The marked lower yield of ML was due to the formation of alkyl glucoside in methanol. Then the reaction was then applied to glucose, fructose, and sucrose, which produced EL in 61, 68, and 62% yield, respectively. The 5-Cl-SHPAO catalyst also catalyzed the transformation of HMF and LA into EL.

Yang et al. (2018) reported the synthesis of glucose-derived amorphous carbon (GC400) as a carbonaceous solid acid catalyst for the preparation of BL from LA. The GC400 catalyst produced BL in a 90.5% yield within 4h at 100 ℃. The excellent catalytic performance of GC400 can be rationalized by its stronger acidity, higher –SO_3H density, and high turnover frequency (TOF) compared to commercially available activated carbon (AC400). The sulfonated carbon GC400 retained 92% of its original catalytic activity even after five cycles.

Huang et al. (2018) reported a metal salt-catalyzed methanolysis of cellulose to ML under microwave irradiation. Among the metal salts screened, $Al_2(SO_4)_3$ showed the best catalytic activity providing ML in 70.6% yield within 40 min at 180 °C. $Al_2(SO_4)_3$ was found to undergo hydrolysis in water and generate both Lewis and Brønsted acids ($[Al(OH)_x(H2O)_y]^{n+}$ and H^+) that facilitated the sequential reaction steps involved in the conversion of cellulose to ML. The reaction was optimized on various reaction parameters, and the catalyst was successfully recycled up to the fifth cycle.

Mulik et al. (2019) prepared a novel heterogeneous catalyst by combining 80:20 physical mixtures of Zr-exchanged PTA and Zr-Beta ($H_2Zr_1PW_{12}O_{40}$+Sn-Beta) for the preparation of EL from glucose. A 54% yield of EL was achieved from glucose (180 °C, 3 h) using 50 wt% of $H_2Zr_1PW_{12}O_{40}$+Sn-Beta loading. The authors explored the role of Sn-Beta and Zr-exchanged PTA, individually on the yield of EL. The Sn-Beta alone could not catalyze the preparation of EL from glucose. However, the $H_2Zr_1PW_{12}O_{40}$ and $HZr_2PW_{12}O_{40}$ catalysts produced EL in 26% and 14% yield from glucose, respectively. The reaction was optimized on temperature, loading of catalyst, and the loading of glucose.

Zhang et al. (2019) developed a series of PTA-based bifunctional catalysts $MPW_{12}O_{40}$ (M=Al^{3+}, In^{3+}, $Cr^{3+,}$ Fe^{3+}) for the direct conversion of carbohydrates into ML. Aluminum phosphotungstate (AlPTA) showed the best catalytic activity in both conventional as well by microwave-assisted heating. A high yield of ML (ca. 64.4%) was obtained from glucose in methanol within 30 min at 160 °C under microwave heating. The methanolysis of glucose was optimized on temperature, time, catalyst, and substrate loading. The optimized conditions were then extended to the methanolysis of other biomass-derived carbohydrates. Fructose, sucrose, and cellulose provided 70%, 65%, and 45% yield of ML, respectively, under identical conditions. The catalyst was successfully recycled and reused up to five cycles.

Kumaravel et al. (2019) reported the synthesis of sulphobenzylated Al-SBA-15 [SO_3H-Bz-AlSBA-15] catalyst for the preparation of EL from LA. In a typical reaction, the sulphonation of benzyl group was performed in various amounts to get nanoporous x% SO_3H-Bz-Al-SBA-15 catalysts (x=0.02, 0.04, 0.06, 0.08 and 0.10 % w/w). Among all the examined catalyst, 0.08% SO_3H-Bz-Al-SBA-15 catalyst showed the best catalytic activity with a 94% yield of EL within 2 h at 80 °C. Then, the esterification of LA over the 0.08% SO_3H-Bz-Al-SBA-15 catalyst was investigated using various alcohols. In optimized conditions, methyl-to-octyl levulinate was produced from LA in excellent (>90%) yields. The catalyst could be recycled and reused up to three cycles without significant loss in catalytic activity.

Liu et al. (2019) reported the esterification of LA into EL using a carbon-based sulfonic catalyst (C-SO_3H). The authors prepared the C-SO_3H catalyst by sulfonating incompletely carbonized sugarcane bagasse. The C-SO_3H catalyst afforded 88.2% yield of EL from LA within 9 h at 120 °C. Furthermore, the reaction was optimized on the reaction temperature, duration, EtOH to LA molar ratio, and the extent of sulfonation on sugarcane bagasse. Then stable C-SO_3H catalyst was successfully recycled and reused up to five times.

2.5 SCOPE OF THE WORK

As evident from the literature survey, there have been significant breakthroughs over the past decade in the production of renewable chemical intermediates like CMF, BMF, and LA by the chemical-catalytic valorization of biomass-derived carbohydrates. There is equal interest in the value-addition of the chemical intermediates into various classes of products of commercial interests. As reported by Mascal et al. (2009), CMF can be isolated in excellent yield by dehydrating carbohydrates within an aqueous HCl-1,2-dichloroethane (DCE) biphasic reaction medium. However, the process requires a large volume of DCE per mole of CMF. The intermittent extractions of CMF make the process lengthy and more challenging. In addition, the process uses low loading of carbohydrates (ca. 1 wt%). High dilution and frequent extraction of CMF are necessary to minimize the decomposition of CMF in the reaction medium. Efforts continue to understand the transformation of carbohydrates into CMF or LA better. According to the literature, the hydroxymethyl group in HMF is protonated and nucleophilically substituted by the chloride or bromide ion to form CMF and BMF, respectively. The transformation can potentially happen both in the aqueous and organic phases. HMF can also decompose into LA or humin by alternative reaction pathways. The distribution coefficient of CMF is highly favored towards the organic phase due to its hydrophobic character. However, CMF can hydrolyze back into HMF in the aqueous layer and participate in reaction pathways leading to humin formation. If the hydrolysis of CMF or the decomposition of HMF into humin can be minimized, the yield of CMF will likely improve. We envisioned that a phase transfer catalyst having chloride ion would increase the chloride ion concentration in the organic phase and slow down the hydrolysis of CMF back into HMF. If the strategy works, it would make the requirement of intermittent extraction of CMF redundant and significantly lower the organic solvent use. In addition, the hydrophobic pocket created by the phase transfer catalyst could favor the transformation of HMF into CMF while minimizing side reactions that lead to the formation of humin. The same logic may be extended to the production of LA directly from carbohydrates through the intermediary of HMF. Quaternary ammonium chlorides could be potential phase transfer catalysts that are relatively stable in aqueous hydrochloric acid. In addition, it is crucial to understand CMF, BMF, and LA's reactivity to explore their derivative chemistries. For example, the halomethyl group in CMF and BMF may be substituted by alkyl alcohols and make 5-(alkoxymethyl)furfurals (AMFs). Alternatively, alkyl levulinates can be prepared by the alcoholysis of CMF or esterification of LA. Alkyl levulinates have potential applications as green solvent, diesel additive, and as a renewable chemical intermediate for further value addition.

2.6 OBJECTIVES

The following objectives have been intended in the present research work based on the above facts and the detailed literature survey.

- To produce CMF and BMF from carbohydrates in the presence of a phase transfer catalyst.
- To study the effect of various cationic surface-active agents on the selectivity and yield of LA starting from carbohydrates.
- To develop a general synthetic methodology in preparing 5-(alkoxymethyl)furfural from biomass-derived CMF and BMF.
- To synthesize levulinic acid esters from biomass-derived CMF, BMF, furfuryl alcohol, and LA using homogeneous and heterogeneous acid catalysts.
- To characterize the synthesized compounds by FTIR, ^{1}H&^{13}C-NMR spectroscopy, and Mass spectrometry.
- To prepare and characterize heterogeneous catalysts by FTIR, SEM-EDX, PXRD, and TGA.

Overall, the present research focuses on the production and synthetic upgrading of CMF, BMF and LA from biomass-derived carbohydrates. The reactions were conducted under conventional heating and magnetic stirring in a batch reactor. This work also explores the derivative chemistries of CMF, BMF, and LA for the synthesis of products of commercial significance. The thesis comprises of seven chapters. **CHAPTER 1** provides a general introduction to the chemocatalytic value addition of cellulosic biomass into fuels and chemicals. A brief literature review, scope of the work, and objectives have been described in **CHAPTER 2**. **CHAPTER 3** analyses the shortcomings in the literature processes of CMF production and proposes a solution to the problem by using quaternary ammonium chloride as a phase transfer catalyst (PTC). The reaction was optimized on the loading of the substrate, type, and loading of PTC, reaction temperature, duration of reaction, and the type of extracting solvent. Noticeably higher yields of CMF were obtained, compared to control when benzyltributylammonium chloride was employed as the PTC. **CHAPTER 4** deals with the efficient and scalable production of LA from biomass-derived sugars and carbohydrates in aqueous hydrochloric acid in the presence of quaternary ammonium chloride as cationic surface-active agent (SAA). The reaction was optimized on the loading of the substrate, type, and loading of SAA, reaction temperature, duration of reaction, and the concentration of hydrochloric acid. **CHAPTER 5** discusses the synthesis of 5-(alkoxymethyl)furfural (AMF) from biomass-derived CMF and BMF in the presence and absence of various inorganic and organic bases additives. The reactions were optimized on various reaction parameters for the best selectivity and isolated yield of AMFs. **CHAPTER 6** discusses the synthesis of a series of alkyl levulinates from biomass-derived furfuryl alcohol, LA, CMF, and BMF using various homogeneous and heterogeneous catalysts. **CHAPTER 7** summarizes the conclusions of results, discusses the outcome of the present research work, and highlights the scope for future work.

CHAPTER 3

PHASE TRANSFER CATALYST ASSISTED ONE-POT SYNTHESIS OF 5-(CHLOROMETHYL)FURFURAL FROM BIOMASS-DERIVED CARBOHYDRATES IN A BIPHASIC BATCH REACTOR

Abstract

In this chapter, the effect of various tetraalkylammonium chloride as phase transfer catalysts (PTC) on the conversion of biomass-derived carbohydrates into CMF has been explored within an aqueous-organic biphasic batch reactor. The process was optimized on temperature, duration, solvent, type, and loading of PTC. The use of benzyltributylammonium chloride (BTBAC) as a PTC led to a roughly 10% increase in the yield of CMF (compared to the control reactions) from all the carbohydrates studied.

3.1 INTRODUCTION

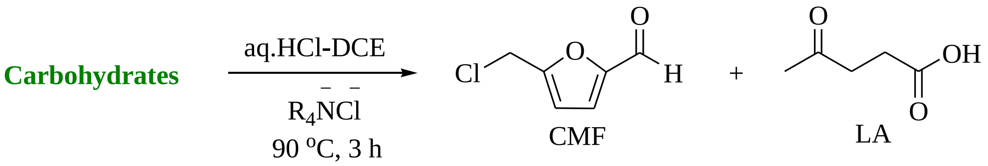
As mentioned in CHAPTER 1, the preparation of CMF was first reported more than a century ago (Fenton et al. 1899, Fenton et al. 1909). With resurging interests in the biorefinery research in the 1990s, CMF as a renewable chemical intermediate has received renewed attention (Fenton et al. 1901, Hamada et al. 2001, Szmant et al. 1981). The number of reports on the preparation and derivative chemistries of CMF and BMF increased exponentially over the past years (Brasholz et al. 2011). Both CMF and BMF have been produced in batch as well as continuous reactors (Gao et al. 2013, Meller et al. 2016). The isolated yield of CMF is significantly influenced by the efficacy in extracting CMF from the aqueous reaction mixture as it forms (Mascal et al. 2008, 2009). Protonation of the hydroxymethyl group in HMF followed by nucleophilic substitution by chloride ion forms CMF (Mascal et al. 2014, Saha et al. 2014, Tahvildari et al. 2011). Due to the hydrophobic character of CMF, its distribution coefficient is favored in most organic solvents (Mascal et al. 2010). However, the interconversion between HMF and CMF can potentially happen in the interface of aqueous and organic layers (Mascal 2019). Hydrolysis of CMF into HMF transports it back into the aqueous layer and exposes it to various degradation pathways (Brasholz et al. 2011, Patil et al. 2012). The strategy to minimize the formation of side products (e.g., LA, humin) from HMF is to keep its concentration as low as possible during the reaction and to convert it into CMF as soon as it forms. The salting-out strategy has been applied successfully for the efficient extraction and isolation of HMF from aqueous or polar reaction media. An increase in the ionic strength of the aqueous/polar reaction medium helps make the distribution coefficient of HMF more favorable in the organic extractant. The polarity and hydrogen-bonding capacity of the organic solvent also plays a crucial role in the partitioning of HMF in between the aqueous and organic layers (Lane et al. 2016). We envisioned that the transformation of HMF into CMF could potentially occur in both aqueous and organic layers. An increase in the chloride ion concentration in both the layers would help to convert HMF into CMF faster and transport it into the organic layer. Besides, a higher concentration of chloride ion in the organic layer would potentially slow down the hydrolysis of CMF into HMF. In this regard, a phase transfer catalyst (PTC) containing chloride counter ion could favor the transformation of HMF to CMF both in the aqueous and organic layer. The selected PTC should be inexpensive, non-toxic, recoverable, and stable under the reaction conditions used. In this work, the effect of various tetraalkylammonium chloride as PTC on the yield and selectivity of CMF has been explored within a biphasic batch reactor. Further, the reaction was optimized on temperature, duration, type of organic solvent, loading of the substrate, and loading of PTC.

3.2 EXPERIMENTAL SECTION

3.2.1 Materials

Microcrystalline cellulose (99%) and benzyltributylammonium chloride (98%) were purchased from Sigma. Hydrochloric acid (35%), chloroform (99%), sodium sulfate (anhydrous, 99%), silica gel (60-120 mesh), D-glucose (99%), D-fructose (99%), sucrose (99%), tetrabutylammonium chloride (98%) and choline chloride (98%) were purchased from Loba Chemie. 1,2-Dichloroethane (98%) was obtained from MolyChem. The round-bottomed glass pressure reactor with the Teflon screw-top (150 mL) was purchased from Sigma Aldrich. Hexadecyltrimethylammonium chloride (HDTMAC) was purchased from TCI, Japan. The chemicals were used as received without further purifications.

3.2.2 Experimental procedure



Scheme 3.1 Production of CMF from carbohydrates using tetraalkylammonium chloride as an additive.

D-Glucose (2 g) was taken in a 150 mL round-bottomed glass pressure reactor fitted with a Teflon screw top. To this, 20 mL of aqueous HCl (35%), DCE (40 mL), and benzyltributylammonium chloride (BTBAC) (0.200 g) were added sequentially. A magnetic stirring bead was added, and the pressure reactor was sealed. The reactor was placed in a pre-heated oil bath (90 °C) the reaction mixture was stirred at 720 rpm for 3 h. After the reaction, the reactor was removed from the oil bath and cooled down to room temperature. The reactor was opened, and the reaction mixture was diluted with ice-cold water (20 mL). The insoluble black solid (*i.e.*, humic matter) was recovered by filtering the reaction mixture, washed with excess water, and then dried in a hot-air oven at 60 °C for several hours till constant weight was obtained. The filtrate was transferred into a separating funnel, and the organic phase was separated. The aqueous phase was extracted with DCE (2×10 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, and the solvent was evaporated in a rotary evaporator under reduced pressure. The orange oil was chromatographed (Silica gel) using chloroform as the eluting solvent. Evaporation of chloroform in a rotary evaporator under reduced pressure provided CMF as yellow liquid (1.032 g, 64%). The aqueous layer was saturated with sodium chloride. The saturated solution was then extracted with ethyl acetate (6×20 mL). The ethyl acetate layers were combined, dried over anhydrous Na_2SO_4, and evaporated in a rotary evaporator under reduced pressure to yield a brown liquid. The liquid was chromatographed over silica gel (60-120 mesh) using ethyl acetate as eluent. Evaporation of the solvent provided LA as light-yellow oil (0.242 g, 19%). The control reactions were performed as described above, except no phase transfer catalyst was used.

3.3 CHARACTERIZATION OF SYNTHESIZED COMPOUNDS

The purity of CMF and LA were confirmed by spectroscopic characterization techniques. Fourier Transform Infrared Spectroscopy (FTIR) is routinely used to identify the functional group(s) present in organic and inorganic materials. FTIR spectra were recorded on a Bruker Alpha 400 FTIR spectrometer, which is equipped with zinc selenide as an IR source. The sample spectra were recorded using the ATR technique. The samples under study were recorded with 24 scans having a sample resolution of 4 cm^{-1}. The ^{1}H-NMR and ^{13}C-NMR spectra is a powerful analytical technique used for both qualitative and quantitative analysis of a product. It helps to identify a molecule by showing characteristic peaks for the bond connectivity. It identifies the chemical environment, neighboring groups present, the relative number of hydrogen atoms, and other NMR-active atoms present in the molecule. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded on 400 and 100 MHz spectrometers using deuterated chloroform as solvent and TMS as an internal standard. Chemical shifts are provided in parts per million and coupling constants in Hertz.

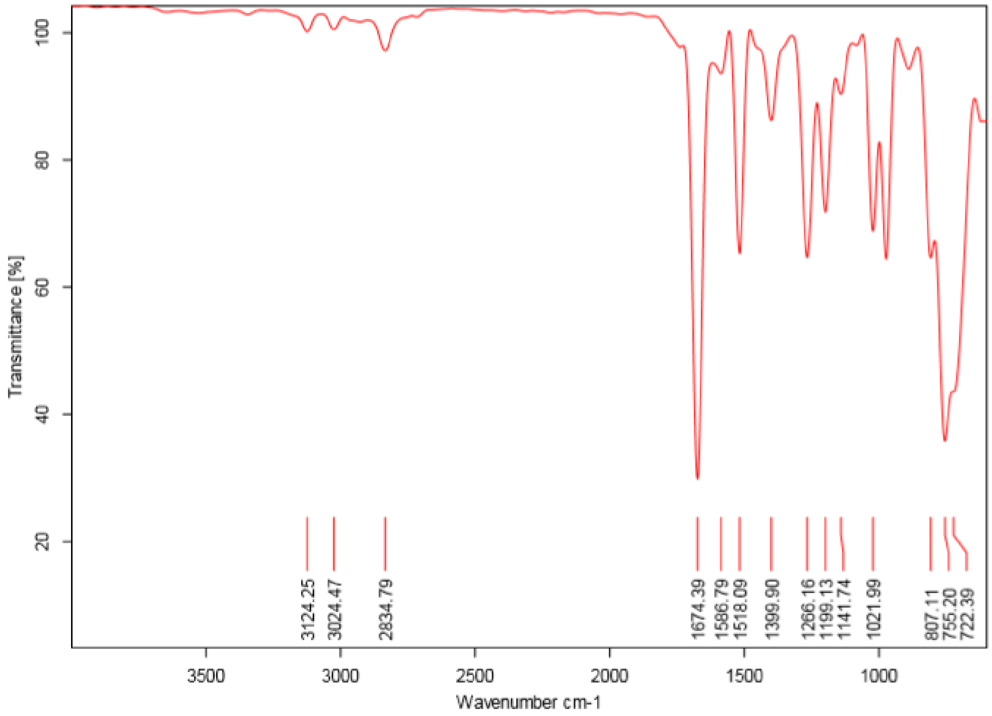


Figure 3.1 The FTIR spectrum of CMF.

FTIR spectroscopy is a powerful tool that provides conclusive ideas about the functional groups present in organic compounds. The peak at 3124 cm^{-1} can be attributed to the =C-H stretch in the furan ring of CMF. The peak around 2834 cm^{-1} shows the stretching vibrations of the methylene (-CH_2) group. The doublet for –C-H in the aldehyde has coincided in the aliphatic region. The strong peak at 1674 cm^{-1} is due to the –C=O stretching frequency of the aldehyde.

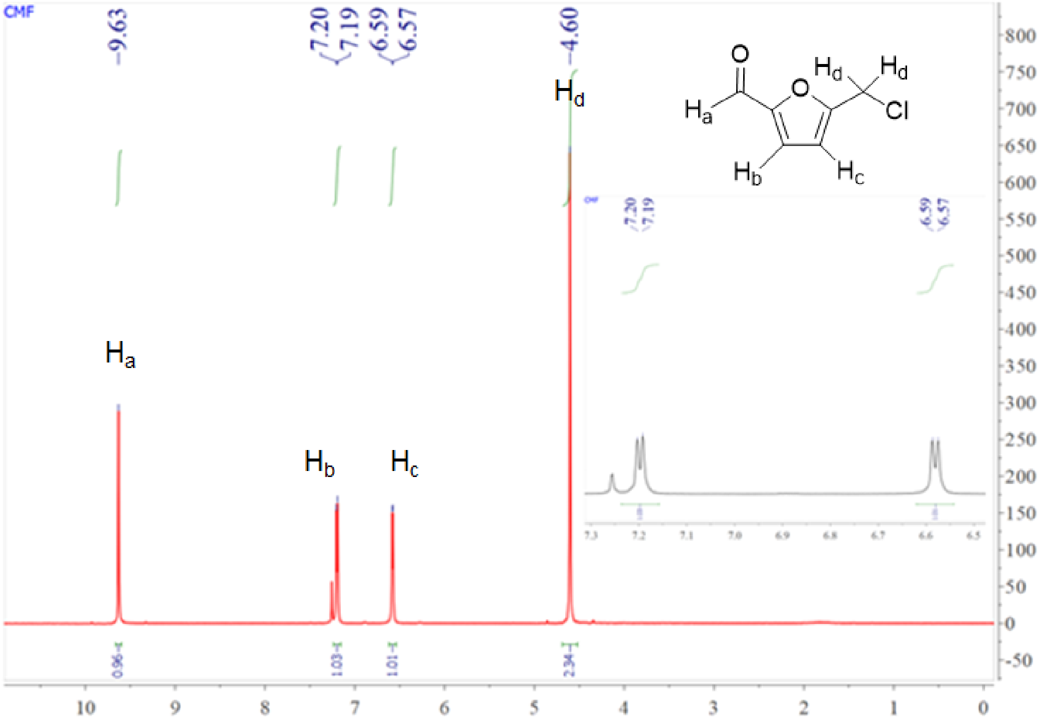


Figure 3.2 The ^{1}H-NMR spectrum of CMF.

The ^{1}H-NMR spectrum of purified CMF shows a singlet at 9.6 ppm due to the aldehyde proton. The doublets at 7.2 ppm and 6.5 ppm represent to the furanic protons. The singlet at 4.6 ppm is due to the methylene protons of the chloromethyl group.

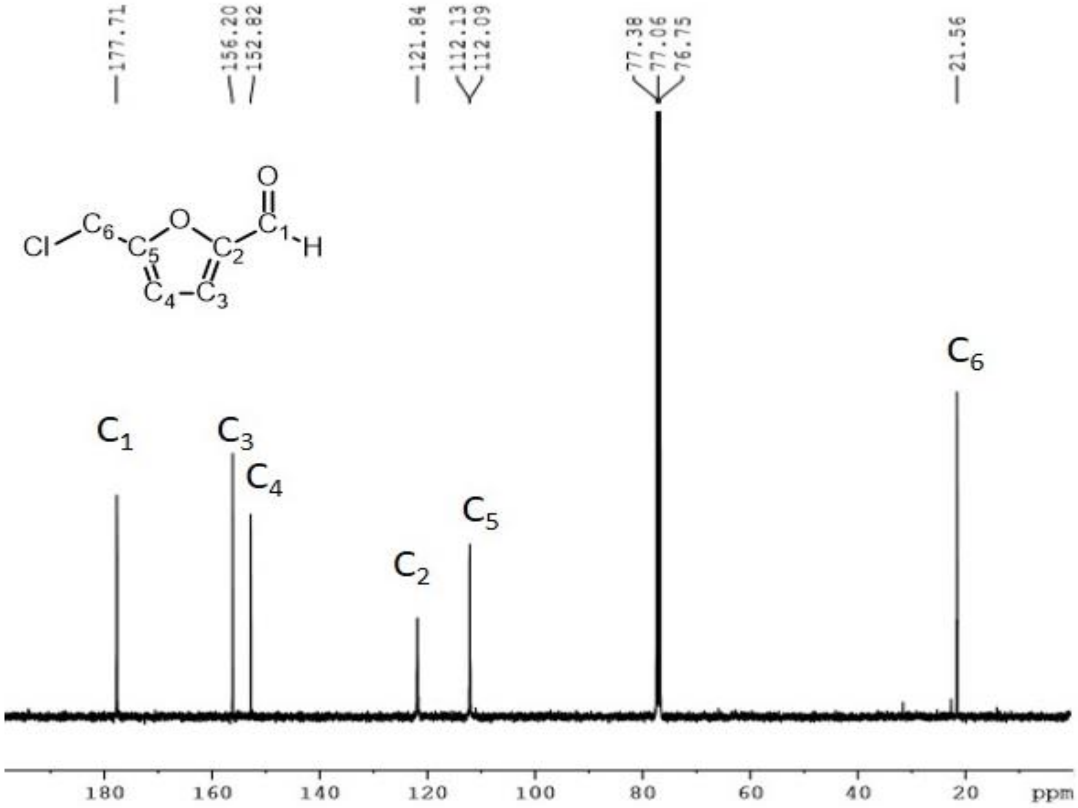


Figure 3.3 The ^{13}C-NMR spectrum of CMF.

^{13}C-NMR of the isolated CMF show the peak at 177.7 ppm is due to the aldehyde carbon (C=O), the four peaks at 156.2, 152.8, 121.8 and 112.1 ppm are corresponding to the furanic carbon atoms. The peak at 21.5 ppm is due to the CH_2 carbon.

3.4 RESULTS AND DISCUSSION

Initially, a slightly-modified literature process of CMF preparation was adopted, and glucose was chosen as the model substrate for the process optimization. In a typical reaction, glucose was suspended in aq. HCl (35%)-DCE biphasic reaction mixture taken in a sealed round-bottomed glass pressure reactor with a Teflon screw top **(Figure 3.4)**. The sealed vessel was placed in a pre-heated oil bath and magnetically stirred during the course of the reaction.

Figure 3.4 Preparation of CMF in a closed batch reactor; snapshots were taken after 5 min (left), 30 min (middle), and 1 h (right).

Initially, the effect of various metal chloride additives on the selectivity and yield of CMF was studied (**Table 3.1)**. Although a marginal increase in the yield of CMF was observed in cases, the effect was not markedly different. The marginal increase in CMF yield compared to the control reactions could be explained by the increase in the ionic strength of the aqueous medium, which helps in extracting HMF into the organic medium. The water-soluble salts could not possibly increase the chloride ion concentration in the organic layer minimizing the hydrolysis of CMF. An efficient catalyst would increase the ionic strength of the medium as well as increase the chloride ion concentration in both the layers. In this regard, tetraalkylammonium chloride as a phase transfer catalyst (PTC) could play an important role. The PTCs would increase relatively free chloride ions in both layers. Therefore, the transformation of HMF to CMF would become faster, whereas the hydrolysis of CMF back into HMF would slow down. The micelle formation could also help protect the reactive intermediates that form during the sugar-to-HMF transformation and help minimize the decomposition reactions that lead to humin formation. The effectiveness of PTC would likely depend on its distribution coefficient. When benzyltributylammonium chloride (BTBAC) was used as the PTC, a significantly higher yield of CMF was obtained compared to the control reaction. Further, the effect of the combination of metal chlorides and PTC like BTBAC were also examined for the CMF synthesis. In contrast to our assumption, the CMF yield decreased. This could be due to the significant interaction of the electrolytes and BTBAC, which decreased the micelle formation from BTBAC. All the yield data were reproduced in triplicate, and the average yield is reported. Intermittent extractions of the DCE layer were avoided to simplify the process and making it a true ‘one-pot' process. The reactions were performed using a relatively high concentration of glucose (ca. 10 wt%), which also increases the commercial attractiveness of the process.

Table 3.1 Influence of various catalyst on CMF yield

Entry	Feedstock	Medium	Additive	Yield of CMF (%)
1	Glucose	HCl-DCE	-	46
2	Glucose	HCl-DCE	1 mL pyridine	46
3	Glucose	HCl-DCE	0.5g LiCl	47
4	Glucose	HCl-DCE	NaCl	44
5	Glucose	HCl-DCE	$MgCl_2$	20
6	Glucose	HCl-DCE	BTBAC/$MgCl_2$	52
7	Glucose	HCl-DCE	$AlCl_3$	50
8	Glucose	HCl-DCE	BTBAC/$AlCl_3$	57
9	Glucose	HCl-DCE	10% (0.2 g) BTBAC	64

Reaction conditions: glucose (2 g), HCl (35%, 20 mL), DCE (40 mL), 90 °C, 3 h.

In addition, LA was isolated in a 15% yield from the aqueous layer. When the reaction was conducted under identical conditions without using BTBAC, CMF and LA were isolated in 46% and 10% yields, respectively. The insoluble humin formation was significantly more in the control reaction. The reaction was then optimized on various reaction parameters, including temperature, duration, nature of solvent, type, and loading of phase transfer catalyst to maximize the yield of CMF.

3.4.1 Effect of various PTC on the yield of CMF

The role of different tetraalkylammonium chloride as PTC on CMF yield was studied, and the distribution coefficients of each PTC were measured and reported in

Table 3.2. Glucose was used as the substrate of choice, and all the PTC were taken at 5.77 mol% of the glucose amount.

Table 3.2 Distribution coefficient of various quaternary ammonium chlorides in a biphasic reaction medium.

Entry	PTC	Amount in DCE (g)	Amount in water (g)	K_d
1	TBAC	0.068	0.432	0.157
2	ChoCl	0.044	0.456	0.096
3	BTBAC	0.120	0.380	0.315
4	BTEAC	0.020	0.480	0.041
5	HDTMAC	0.017	0.483	0.035

Reaction conditions: quaternary ammonium salts (0.5g), DCE (10 mL), HCl (6M, 10 mL) and stirred magnetically for 1 h at RT.

Use of tetrabutylammonium chloride (TBAC) as PTC provided CMF in 50% yield against 46% in the control reaction. The effect may be explained by the highly favored distribution coefficient of TBAC towards the aqueous layer that renders it inefficient in slowing down the hydrolysis of CMF into HMF in the organic layer (Entry 1). When choline chloride (ChoCl) was used as PTC, CMF was obtained in 50% yield only. The use of hexadecyltrimethylammonium chloride (HDTMAC) as a PTC lowered the yield of CMF below the control reaction, and CMF was isolated in only 30% yield. Significantly more humin was isolated in the process. The lower yield of CMF may be explained by the lower distribution coefficient of HDTMAC in the DCE layer (Entry 5). Besides, the surfactant molecule produced lathers in the reaction mixture that possibly accelerated side reactions. On the contrary, when BTBAC was used as PTC, CMF was isolated in 64% yield. This significantly higher yield of CMF can be explained by the much higher distribution coefficient of BTBAC is the DCE phase (Entry 3). CMF in the DCE layer was effectively shielded from further decomposition reactions. The effect of various quaternary ammonium chloride PTCs on the yield of CMF has been depicted in **Figure 3.5**.

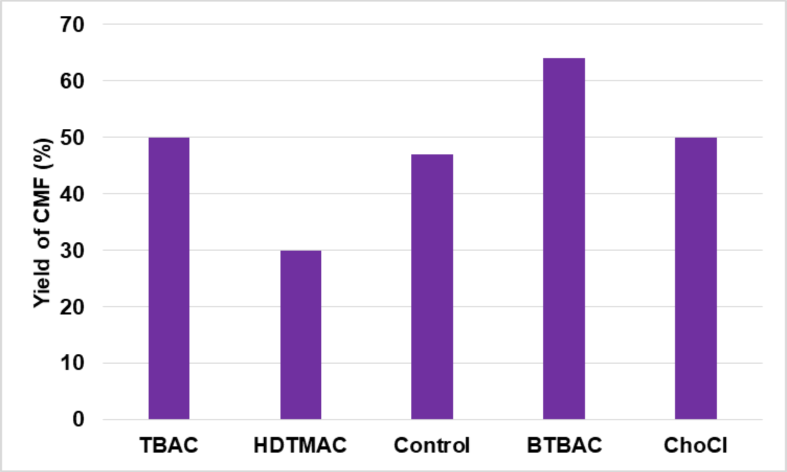


Figure 3.5 Effect of various tetraalkylammonium chloride as a phase transfer catalyst on the yield of CMF.

Reaction conditions: glucose (2 g), HCl (35%, 20 mL), DCE (40 mL), PTC (5.77 mol%), 90 °C, 3 h.

Since BTBAC was found to be the best PTC for the CMF synthesis, the effect of its loading on the yield of CMF was studied. The loading of BTBAC was varied from 5 wt% to 30 wt% with respect to the weight of glucose used in the reaction **(Figure 3.6)**. At lower loadings (<10 wt%) of BTBAC, the increase in yield of CMF compared to the control reaction was not pronounced. However, when the loading was increased by more than 10 wt% (5.77 mol%), the yield of CMF remained unaltered. Therefore, the optimized loading of BTBAC was kept at 10 wt% of the glucose amount.

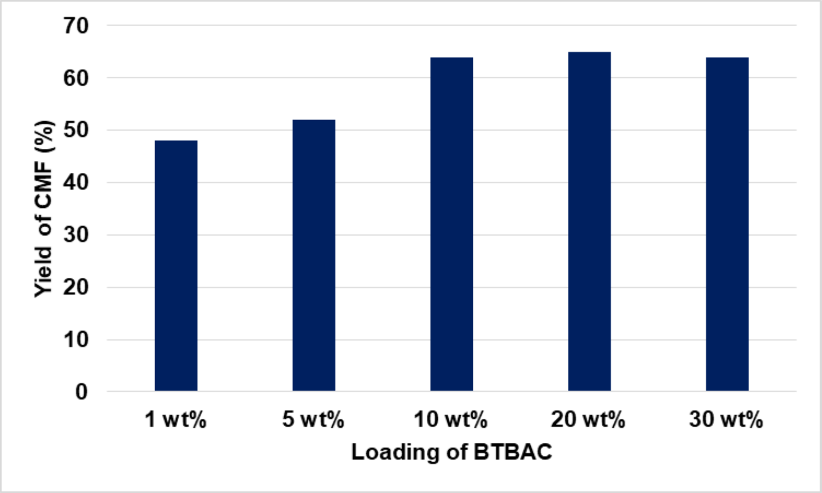


Figure 3.6 Effect of the loading of BTBAC on the yield of CMF.

Reaction conditions: glucose (2 g), HCl (35%, 20 mL), DCE (40 mL), 90 °C, 3 h.

3.4.2 Effect of reaction temperature and time on the yield of CMF

The reaction temperature is an important parameter for the optimization of CMF yield. When the reaction was conducted at 80 °C for 3 h, only 47% of CMF yield observed. On the other hand, increasing the reaction temperature to 100 °C provided a 48% yield of CMF. At 90 °C maximum 64% yield of CMF obtained from the glucose. The reason for the lower yield of CMF at higher temperatures is due to higher rate decomposition of CMF during the reaction, whereas a decrease in CMF yield at a lower temperature can be attributed to the incomplete reaction. Hence the optimized reaction condition could be 90 °C for the synthesis of CMF from glucose **(Figure 3.7)**.

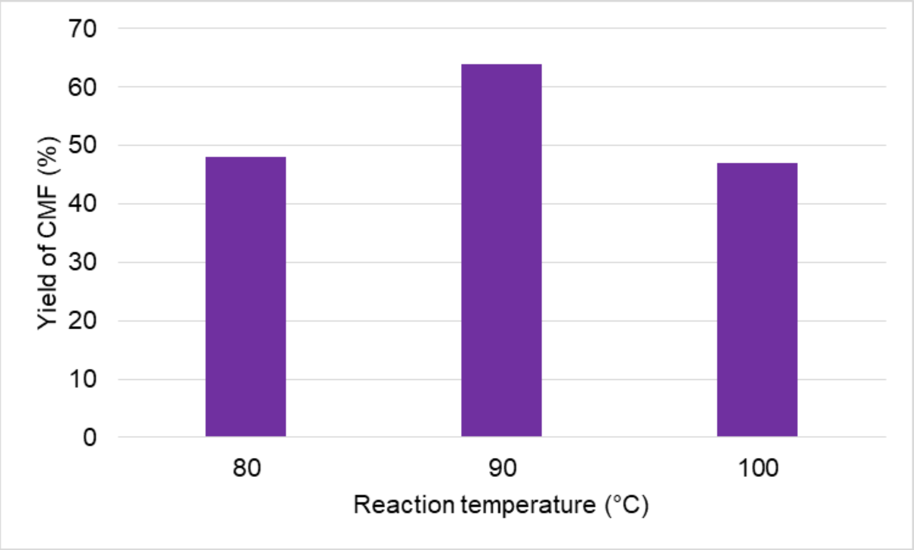


Figure 3.7 Effect of reaction temperature on the isolated yield of CMF.

Reaction conditions: glucose (2 g), HCl (35%, 20 mL), DCE (40 mL), BTBAC (0.2 g, 10 wt%), 3 h.

The reaction duration also has a significant role in the synthesis of CMF from carbohydrates. Hence the reaction was then optimized on the duration using glucose as the substrate. When the reaction was conducted at 90 °C for 2 h only, CMF was isolated in only a 28% yield. Conducting the reaction for longer than 3 h also lowered the yield of CMF. For example, CMF was isolated in only a 50% yield when the reaction was conducted at 90 °C for 4 h. The lower yield of CMF at 2 h reaction time may be attributed to incomplete conversion of glucose, whereas the lower yield of CMF for longer duration may be the decomposition of CMF due to the longer exposer of CMF formed in aqueous acid present in the reaction mixture. Hence the optimized reaction duration for the efficient synthesis of CMF is 3 h **(Figure 3.8)**.

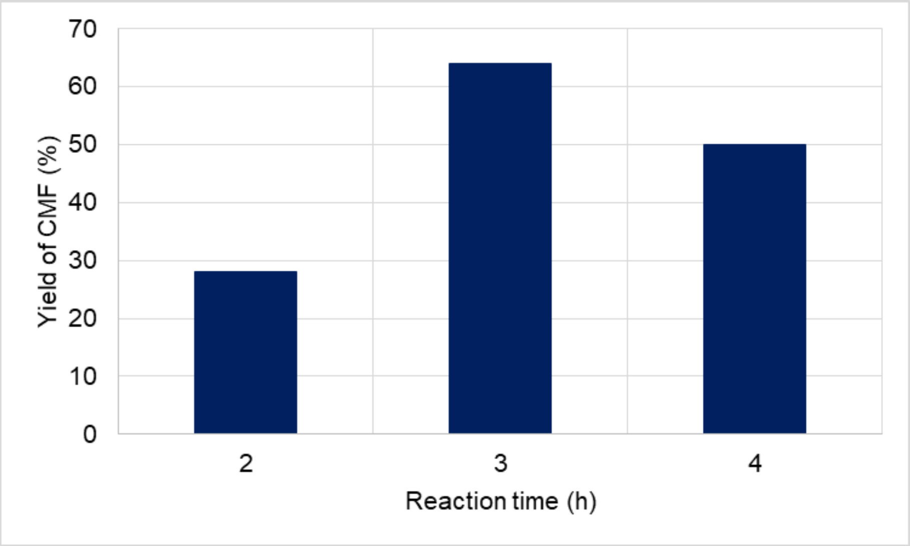


Figure 3.8 Effect of reaction time on the CMF yield.

Reaction conditions: glucose (2 g), HCl (35%, 20 mL), DCE (40 mL), BTBAC (0.2 g, 10 wt%), 90 °C.

3.4.3 The efficiency of the extracting solvent

The yield of CMF is significantly influenced by the efficacy of extracting CMF into the organic phase. The organic solvent plays an important role in the process since it extracts CMF from the aqueous acid as it forms and shields it from decomposition reactions. Hence, in the present work, the effect of various organic solvents, frequently used in the literature for the synthesis of CMF, has been examined. Using glucose as the substrate of choice, the effect of toluene, DCE, chloroform, and chlorobenzene as extracting solvent was studied. The extraction experiments revealed that Chlorinated solvents such as chloroform and DCE were found to be the most effective solvent provided CMF in 42% and 64% isolated yield, respectively. Toluene performed poorly with less than 20% yield of CMF, whereas chlorobenzene was found to be as effective as DCE and provided CMF in a 60% yield. The trend can be correlated with increasing dielectric constant (hydrogen bonding capacity and polarity) of the solvents increasing from toluene to chloroform to chlorobenzene to DCE. A solvent with more dielectric constant extracts HMF and CMF from the aqueous medium into the organic medium more efficiently and shields them from further decomposition in aqueous acid **(Figure 3.9)**.

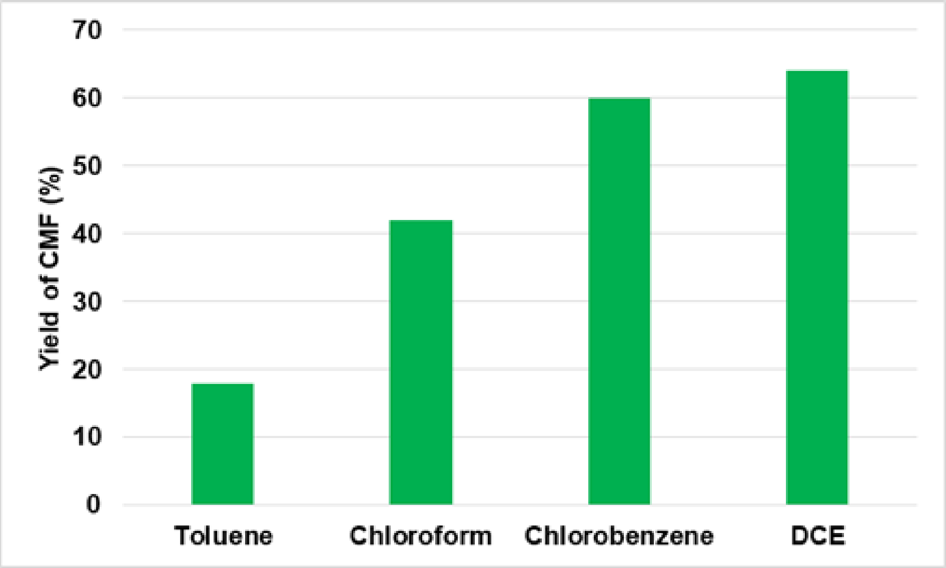


Figure 3.9 Effect of solvent on the isolated yield of CMF.

Reaction conditions: glucose (2 g), HCl (35%, 20 mL), solvent(40 mL), BTBAC (0.2 g, 10 wt%), 90 °C, 3 h.

3.4.4 Effect of stirring rate on CMF yield

Since the reaction is in the biphasic system, it is essential to maintain a mass transfer between phases. Thus, the stirring rate effect was studied under the optimized conditions using glucose as a substrate. It was observed that at lower stirring rates, the CMF yield decreased. This observation may be due to the lower rates of mass transfer between the phases, which leads to other decomposition pathways. A similar effect is observed in the case of magnetic stirring at high rpm. A moderate stirring speed (ca. 720 rpm) was found optimum for a high isolated yield of CMF. Thus, a moderate stirring rate (720 rpm) is the optimized stirring rate recommended for the synthesis of CMF in high yield.

3.4.5 Conversion of various carbohydrates into CMF

The optimized reaction conditions were then applied to various carbohydrates for the production of CMF. Control reactions were conducted for each substrate and compared with reaction using BTBAC as PTC. In the presence of 10 wt% of BTBAC, glucose provided CMF in 64% isolated yield, whereas the control reaction provided only 46% CMF under identical conditions. Fructose provided 62% yield of CMF in the presence of BTBAC, whereas the control reaction provided CMF in 53% isolated yield. Sucrose provided the best yield of CMF at 73%, whereas the control reaction provided a 59% yield. Microcrystalline cellulose provided CMF in 48% yield with BTBAC but afforded only a 36% yield without the BTBAC additive. CMF was isolated in 42% yield from starch in the presence of 10 wt% BTBAC, whereas only 28% CMF was obtained in the control reaction **(Figure 3.10)**.

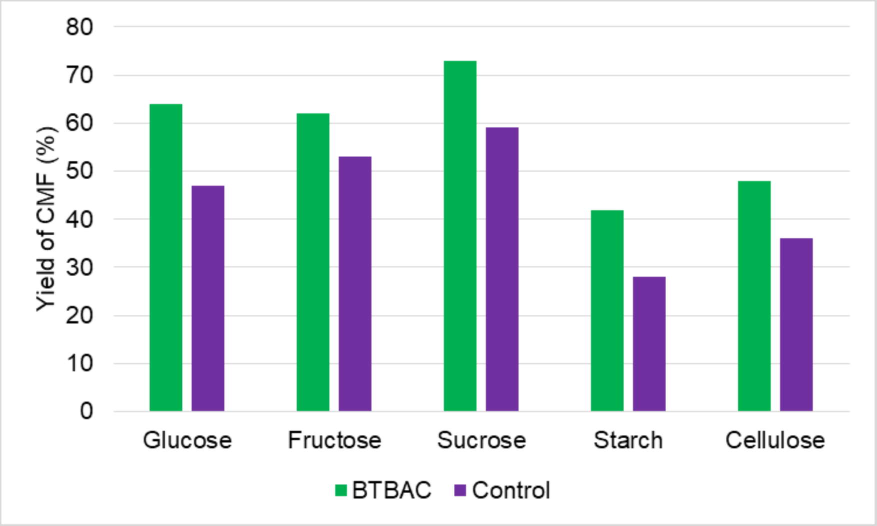


Figure 3.10 Yields of CMF from various carbohydrates in the presence and absence of BTBAC as the phase transfer catalyst.

Reaction conditions: carbohydrate substrate (2 g), HCl (35%, 20 mL), DCE (40 mL), 90 °C, 3 h, BTBAC (0.2 g).

In all the reactions, LA and the insoluble humic matter were isolated from the aqueous layer and quantified. Fructose provided a 14% yield of LA (with BTBAC) against 12% of LA in the control reaction (without BTBAC). Glucose provided 15% yield of LA in the presence of BTBAC, whereas the control reaction provided only 10% yield of LA. The humic matter in the control reaction was also found to be marginally higher than the reaction using BTBAC. When sucrose was used as the substrate, LA was isolated in 11% yield. Starch and cellulose provided 13% and 15% of LA, respectively. Therefore, in all cases, LA was obtained in marginally higher yields using

BTBAC as the PTC. The combined higher yields of CMF and LA using BTBAC is also reflected by less humic matter formation. For example, the humic matter recovered from sucrose using BTBAC was noticeably lower than that obtained from the control reaction **(Table 3.3, Entry 3)**.

Table 3.3 Formation of LA and humic matter from various carbohydrates with or without using BTBAC

S/N	Feedstock	With BTBAC		Without BTBAC	
		LA(%)	Humic matter (g)	LA(%)	Humic matter (g)
1	Glucose	15	0.170	10	0.183
2	Fructose	14	0.182	12	0.200
3	Sucrose	11	0.124	8	0.197
4	Starch	13	0.250	10	0.320
5	Cellulose	15	0.280	9	0.340

Lower loading of the substrate provided better yields of CMF. For example, when the loading of glucose was lowered to 5 wt%, the yield of CMF increased to 68%. This result can be explained by fewer condensation reactions between the intermediates (e.g., HMF) and is well-documented in the literature (Mascal et al. 2009). When a higher quantity of DCE was used (ca. 80 mL), CMF was isolated in a marginally higher yield. With glucose as the substrate, the use of 80 mL of DCE provided CMF in a 69% yield against 64% in the presence of 40 mL of DCE.

3.4.6 Catalyst recovery and recyclability

Recyclability of the catalyst is one of the important parameters for the green indices and process economics. Hence the BTBAC catalyst is recovered from the silica gel column of CMF by eluting with 20% methanol in chloroform, where 96% of BTBAC has been retrieved effectively. Then the efficiency of the recovered catalyst tested for the CMF synthesis from glucose under identical conditions. After the reaction, only 53% of CMF was obtained. The relatively lower yield of CMF may be attributed to the decreased efficiency of the catalyst. Further, the ^{1}H-NMR spectrum of the recovered catalyst confirmed partial decomposition of the catalyst. The chloride ion attacked BTBAC and formed benzyldibutylammonium chloride, and butyl chloride. BTBAC was ineffective in improving the yield of BMF as there was nearly no change in the yield of BMF in the presence or absence of BTBAC. The result may be explained by the faster decomposition of BTBAC by the more nucleophilic bromide anion. Hence, we get only 36% of BMF from glucose in HBr-DCE biphasic medium in the presence of BTBAB (Benzyltributylammonium bromide) under identical conditions.

3.5 CONCLUSION

A one-pot production of CMF has been achieved in a biphasic closed batch reactor consisting of aqueous HCl and DCE in the presence of BTBAC as a phase transfer catalyst. The use of BTBAC afforded CMF in roughly 10% higher yields from all the carbohydrates studied. LA was also isolated in marginally higher yields in reactions using BTBAC compared to the control reactions. The humic matter formed in noticeably lower quantities in reactions using BTBAC. The process maximizes the substrate loading up to 10 wt% with a significant reduction of the total volume of organic solvent used in the process compared to the existing literature processes.

CHAPTER 4

CATALYTIC CONVERSION OF BIOMASS-DERIVED CARBOHYDRATES INTO LEVULINIC ACID ASSISTED BY A CATIONIC SURFACE-ACTIVE AGENT

Abstract

In this chapter, the direct conversion of biomass-derived carbohydrates into LA was investigated using various quaternary ammonium salts as cationic surface-active agent (SAA). Then relative efficiency of SAA has been carried out in the presence and absence of SAA in aqueous hydrochloric acid media. The reaction has been optimized on the reaction temperature, duration, the concentration of hydrochloric acid, type, and loading of the SAA used. The use of benzyltributylammonium chloride (BTBAC) as an SAA increased the yield of LA by 8-17% when compared to the control reaction.

4.1 INTRODUCTION

As discussed in CHAPTER 1, LA is at the forefront of the biorefinery revolution (Garcés et al. 2017, Girisuta et al. 2006, Melero et al. 2012). Hundreds of publications and patents over the past three decades have been dedicated to the production and value addition of LA as a biorenewable chemical building block (Antonetti et al. 2016, Pileidis et al. 2016). Some of the derivative chemistries of LA are well-documented and commercially attractive (Braden et al. 2011, Ismalaj et al. 2014, Zhang 2016). However, the bottleneck of these processes remains to be the commercial viability in producing LA from inexpensive biomass feedstock (Mascal 2019, Morone et al. 2015, Román-Leshkov et al. 2006). Among hundreds of processes of producing LA from biomass, two processes stand out from the rest in terms of the scalability of the process and the high isolated yield of LA. The Biofine^{TM} process uses a two-stage process in converting the hexose content of biomass to LA. In the first stage, the carbohydrates are hydrolyzed to HMF at 220 °C and only 15 s of residence time in a plug flow reactor using dilute sulfuric acid. In the second reactor, the HMF is rehydrated and ring-opened to LA and formic acid at a relatively lower temperature (ca. 190 °C) but longer residence time (ca. 15 min). LA was recovered by vacuum distillation of the reaction mixture (Hayes et al. 2006, Kamm et al. 2006). However, recovery of the sulfuric acid catalyst was challenging. In 2008, Mascal et al. reported a two-step synthesis of LA, where the biomass feedstock is first converted into CMF within a biphasic batch reactor. In the second step, CMF is rehydrated to LA in excellent yield. However, the production of CMF requires concentrated HCl and require special apparatus for its use. Hydrolysis of

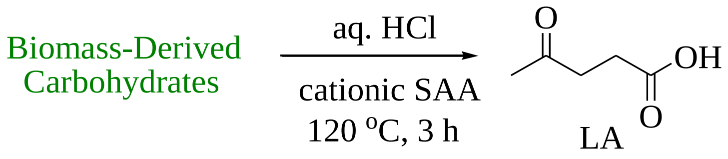
CMF forms a dilute solution of HCl that has to be concentrated to make more CMF. In both the above processes, the yield of LA reached as high as 80% of the theoretical amount (Mascal et al. 2008, 2009, 2010). However, both processes use relatively low loading of biomass and require multiple steps for the isolation of LA. Besides, both reactions use relatively harsh conditions, and the formation of insoluble humic matter cannot be avoided. In this regard, a one-pot production of LA from biomass or biomass-derived carbohydrates under relatively milder conditions would be preferred. Needless to say, if the number of side reactions during LA synthesis or the decomposition of HMF into the humic matter can be minimized, the yield of LA would improve (Hegner et al. 2010). Therefore, there is significant interest in developing a simple but elegant process that enables producing LA in high selectivity and yield under relatively mild conditions. We envisioned that the use of surface-active agents (SAA) shields the side reactions that take place in LA synthesis. Interestingly, the hydrophobic pocket of SAA preserves the LA from other decomposition pathways. In this chapter, the production of LA from biomass-derived carbohydrates using azeotropic HCl (20.2% HCl) under relatively mild reaction conditions is reported. The azeotrope allowed higher reaction temperatures to be achieved without the loss of HCl by degassing. The azeotrope also allowed sequential removal of aqueous hydrochloric acid (without altering the acid composition), and LA by fractional distillation. In the present work, we employed various quaternary ammonium salts as cationic SAA. The relative efficiency of SAA has been carried out in the presence and absence of SAA. Then the reaction has been optimized on the reaction temperature, duration, the concentration of hydrochloric acid, type, and loading of the SAA used.

4.2 EXPERIMENTAL SECTION

4.2.1 Materials

Microcrystalline cellulose (99%) and benzyltributylammonium chloride (98%) were purchased from Sigma. Hydrochloric acid (35%, aq.), anhydrous sodium sulfate (99%), silica gel (60-120 mesh), glucose (99%), fructose (99%), sucrose (99%), tetrabutylammonium chloride (98%) and choline chloride (98%) were purchased from Loba Chemie. The glass pressure reactor with a Teflon screw top (100 mL) was purchased from Sigma Aldrich. Hexadecyltrimethylammonium chloride (HDTMAC) was purchased from TCI, Japan. All the chemicals were used as received without further purification.

4.2.2 Experimental procedure



Scheme 4.1 Preparation of LA from carbohydrates in aqueous hydrochloric acid in the presence of a cationic SAA.

D-Glucose (2.002 g) was taken in a 100 mL round-bottomed glass pressure reactor fitted with a Teflon screw top. To this, aqueous HCl (20.2%, 40 mL) and benzyltributylammonium chloride (0.200 g) were added. A magnetic stirring bead was added, and the pressure reactor was sealed. The reactor was placed in a pre-heated oil bath (120 °C), and the reaction mixture was stirred at 720 rpm for 3 h. After the reaction, the reactor was removed from the oil bath and cooled down to room temperature. The reactor was opened, and the reaction mixture was filtered through a Whatman filter paper under vacuum, and the black humic solid on the filter paper was washed with water (10 mL). The filtrate was saturated with NaCl and cooled in an ice bath. The cold solution was extracted with ethyl acetate (6×20 mL). The ethyl acetate layers were combined, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure in a rotary evaporator. The crude reddish-brown liquid was chromatographed over silica gel (60-120 mesh) using ethyl acetate as eluent. Evaporation of ethyl acetate provided LA (1.032 g, 80%) as light yellow oil. The control reactions were performed as described above, except no phase transfer catalyst was used. The insoluble black solid (humin) left on the filter paper was washed with distilled water and then dried in a hot-air oven at 60 °C overnight till constant weight was obtained.

4.3 CHARACTERIZATION OF SYNTHESIZED COMPOUNDS

The synthesized LA was characterized by FTIR, ^{1}H-NMR, and ^{13}C-NMR spectroscopic analysis, as mentioned in **Section 3.3** of CHAPTER 3.

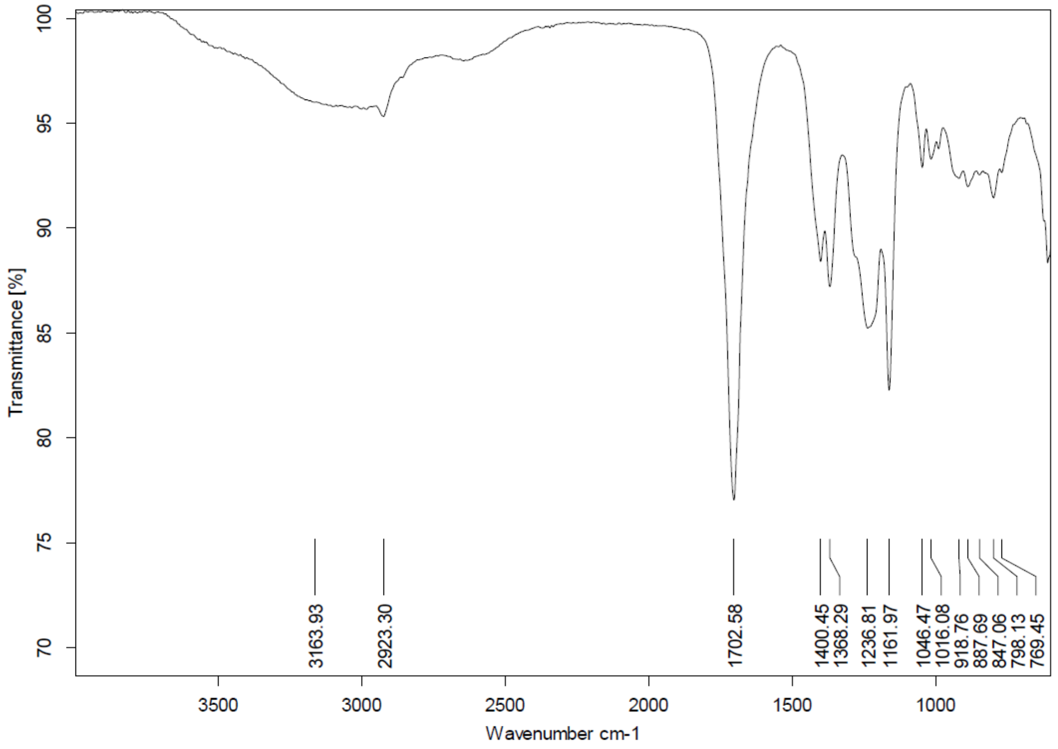


Figure 4.1 The FTIR spectrum of LA

The peak at 3163 cm^{-1} is responsible for the –OH stretching of the carboxylic acid. The peaks around 2923 cm^{-1} are attributed to the sp^{3} –CH stretching vibrations, and the peak at 1702 cm^{-1} is due to the –C=O (carbonyl) stretching vibration. The peak at 1236 and 1161 cm^{-1} correspond to the –C-O stretching frequency of carboxylic acid.

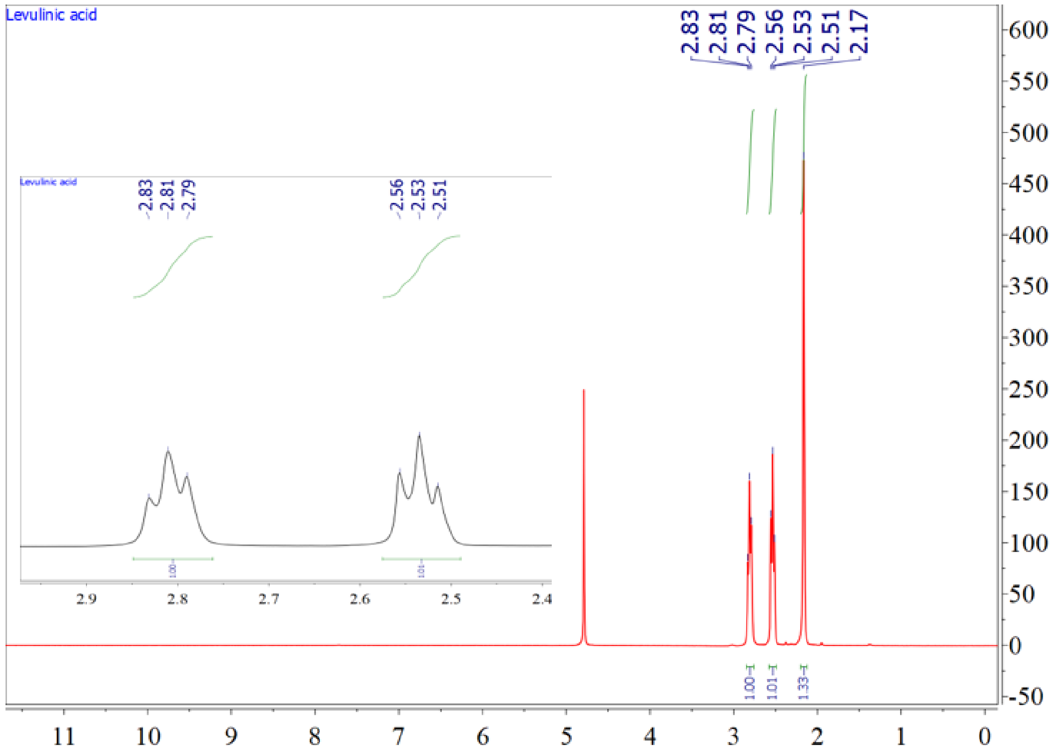


Figure 4.2 The ^{1}H-NMR spectrum of LA.

The ^{1}H-NMR of the isolated LA in D_2O shows a singlet at 2.17 ppm (3H) due to the methyl group attached to the ketone. Two triplets at 2.81 ppm (2H) and 2.51 ppm (2H) are due to the two methylene groups in LA.

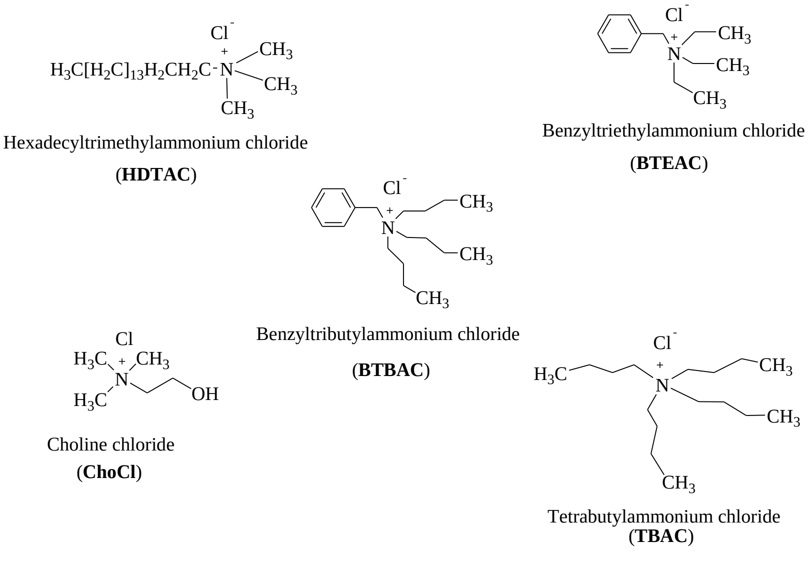
Signals at 206.8 and 177.9 ppm in the ^{13}C-NMR spectrum of LA correspond to the carbonyl carbon atoms in the ester and ketone group, respectively. The two peaks at 37.7 and 29.8 attributed to the two methylene carbons. The peak at 27.7 corresponds to the methyl group attached to the ketone.

4.4 RESULTS AND DISCUSSION

As discussed in CHAPTER 3, the use of BTBAC as a PTC significantly improved CMF yield compared to the control reaction. Interestingly, the yield of LA was also noticeably higher in reactions using BTBAC. This observation motivated us to employ BTBAC for the direct synthesis of LA from the biomass-derived carbohydrates. Therefore, the present work reports the preparation of LA from biomass-derived carbohydrates in aqueous hydrochloric acid employing BTBAC as a cationic surface-active agent (SAA). The reactions were conducted in a batch-type reactor using the azeotropic concentration of hydrochloric acid (20.2% HCl). Glucose, being an inexpensive and abundant feedstock, was chosen as the model substrate for the process optimization in preparing LA. In a typical reaction, glucose (2.002 g) was dissolved in 20.2% aqueous hydrochloric acid (40 mL), and BTBAC (0.2 g, 5.77 mol%) was added. The homogeneous solution was taken in a glass pressure reactor and magnetically stirred at 120 °C for 3 h. LA was isolated from the aqueous solution by extracting with ethyl acetate or by distilling out the aqueous acid under reduced pressure. The control reactions were carried out using identical reaction conditions, except no BTBAC was added. All the experiments were performed in triplicate, and the average yield is being reported. The mass balance is the form of insoluble humin was also measured in every reaction.

4.4.1 Effect of various SAA on LA yield

The effect of various quaternary ammonium chlorides as SAA on the isolated yield of LA was examined using glucose as the model substrate. Five commercially-available quaternary ammonium chlorides having different chain length and distribution coefficients were examined **(Figure 4.3)**.



Hexadecyltrimethylammonium chloride (**HDTAC**)

Benzyltriethylammonium chloride (**BTEAC**)

Benzyltributylammonium chloride (**BTBAC**)

Choline chloride (**ChoCl**)

Tetrabutylammonium chloride (**TBAC**)

Figure 4.3 Structures of various quaternary ammonium chlorides used as SAA additive in LA preparation.

The control reaction without SAA afforded 64% yield of LA. When tetrabutylammonium chloride (TBAC) was used as the SAA, the yield of LA increased significantly to 74% **(Figure 4.4)**. When hexadecyltrimethylammonium chloride (HDTMAC) and choline chloride (ChoCl) were used as SAA, LA was obtained in 71% and 69% yield, respectively. BTBAC was found to be the best SAA that afforded LA in an 80% isolated yield. The trend can be correlated with the distribution coefficient of the SAA used. With the more non-polar character of the SAA, the yield of LA increases. With shorter alkyl chain length, benzyltriethylammonium chloride (BTEAC) provided LA in 67% yield.

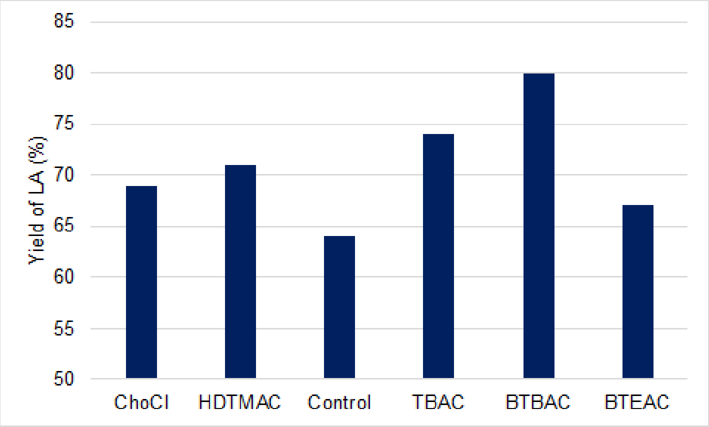


Figure 4.4 Preparation of LA from glucose using various SAA.

Reaction conditions: D-glucose (2.002 g), SAA (5.77 mol%), HCl (20.2% aq., 40 mL), 120 °C, 3 h.

Since BTBAC was found to be the most effective SAA in the preparation of LA, the effect of the loading of BTBAC on the yield of LA was examined. The loading of BTBAC was varied from 5 wt% to 15 wt% with respect to the weight of glucose used in the reaction **(Figure 4.5)**. When the loading of BTBAC was decreased to 5 wt% of glucose, LA was isolated in 70% yield, marginally higher than that in the control reaction. Increasing the BTBAC loading to 10 wt% of glucose, LA was isolated in 80% yield. However, increasing the loading of BTBAC to 20 wt% of glucose did not improve the yield of LA. Therefore, the optimized loading of BTBAC was kept at 10 wt% of the glucose amount used.

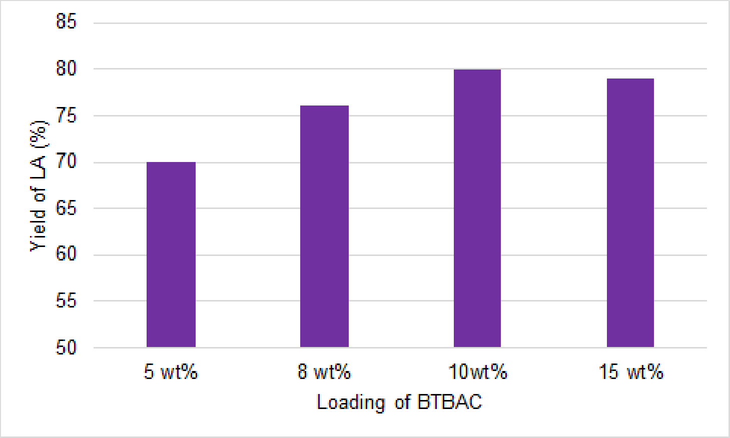


Figure 4.5 Effect of the loading of BTBAC on the yield of LA.

Reaction conditions: Glucose (2.002 g), HCl (20.2%, 40 mL), 120 °C, 3 h.

4.4.2 Effect of reaction temperature on LA yield

The reaction temperature plays an important role in the conversion of glucose and the selectivity of LA. According to the mechanistic details, elevated temperature favors rehydration of HMF and ring-opening to LA. When the reaction was conducted at 100 °C for 3 h, only 47% of LA yield observed **(Figure 4.6)**. Increasing the reaction temperature to 110 °C provided a 68% yield of LA. At 120 °C, a maximum 80% yield of LA obtained from glucose. Decreased yields at lower temperatures can be explained by the incomplete conversion of glucose or HMF into LA. When the reaction was conducted at 130 °C, the yield of LA decreased to 70%. The result can be rationalized by the decomposition of LA at elevated temperatures.

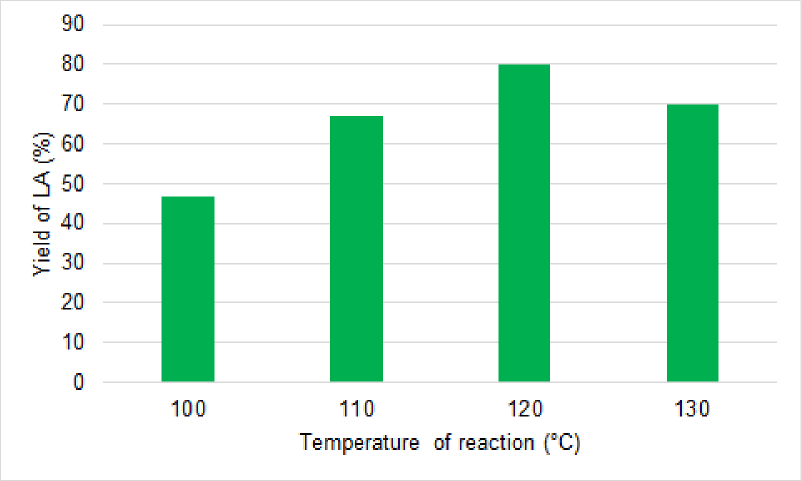


Figure 4.6 The effect of reaction temperature on the yield of LA.

Reaction conditions: D-glucose (2.002 g), BTBAC (5.77 mol%), HCl (20.2%, 40 mL), 3 h.

4.4.3 Effect of acid concentration on LA yield

The present work employed azeotropic hydrochloric acid for the production of LA from glucose. The acid solution allowed higher temperatures to be achieved without the loss of hydrogen chloride by degassing. The azeotrope also allowed the removal of aqueous hydrochloric acid by distillation without changing the acid composition and subsequent isolation of LA. The effect of HCl concentration on the yield of LA in the range of 4-8N was studied. The use of 6N HCl (20.2%) provided the best yield (i.e., 80%) of LA **(Figure 4.7)**. Whereas 4N HCl provided LA in 71% yield, 8N HCl provided LA in a 69% yield. The yields of LA at 5N and 7N HCl were slightly lower than those at 6N HCl. The lower yield of LA at higher concentrations may be attributed to a higher rate of side reactions and decomposition of LA formed. Lower yields of LA at lower concentrations of HCl may be due to incomplete reactions.

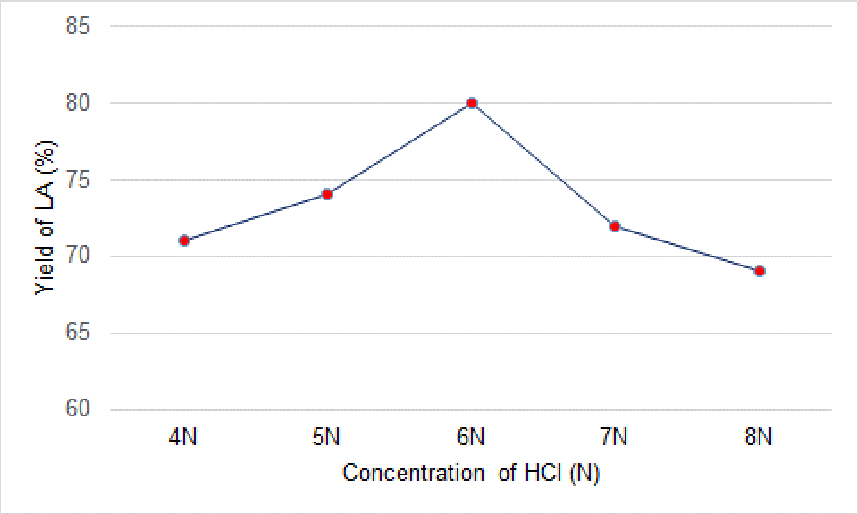


Figure 4.7 Effect on the hydrochloric acid concentration on the isolated yield of LA.

Reaction conditions: D-glucose (2.002 g), BTBAC (5.77 mol%), aq. HCl (40 mL), 120 °C, 3 h.

4.4.4 Conversion of various biomass-derived carbohydrates into LA

The optimized reaction condition for the production of LA from glucose was then extended to other biomass-derived carbohydrates. The reactions were carried out at 120 °C for 3 h using 2.002 g of substrate, 5.77 mol% of BTBAC, and 40 mL of aqueous HCl (6N). The control reactions were also carried out under identical conditions, except no BTBAC was added to the reaction mixture. When glucose was used as the substrate, the yield of LA reached 80% using 5.77 mol% of BTBAC, whereas the control reaction provided only 64% of LA. Fructose provided 76% of LA in the presence of BTBAC, whereas the control reaction provided only 59% of LA. When sucrose was used as the substrate, LA was isolated in 74% and 66% yield in the presence and absence of BTBAC, respectively. Polymeric carbohydrates such as starch and cellulose provided lower yields of LA compared to the sugars. Microcrystalline cellulose gave a 68% yield of LA in the presence of BTBAC, which was otherwise isolated in 60% yield in the control reaction. Soluble starch provided LA in 57% yield in the control reaction that increased up to 66% yield in the presence of 5.77 mol% of BTBAC as a cationic SAA **(Figure 4.8)**.

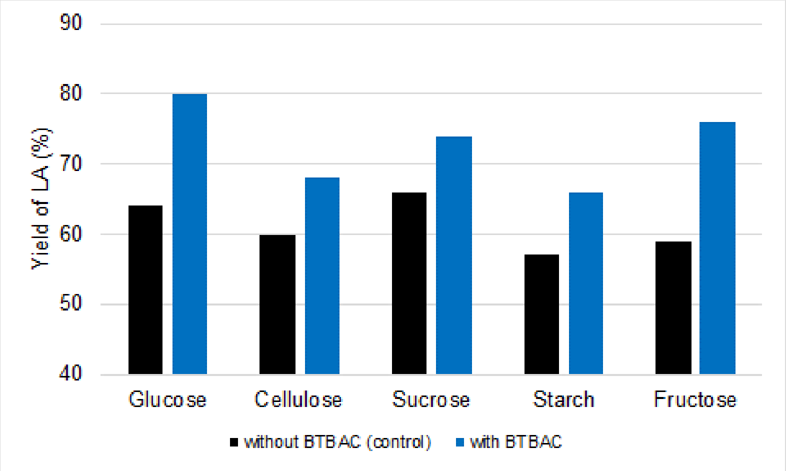


Figure 4.8 Preparation of LA from various carbohydrate feedstocks.

Reaction conditions: Substrate (2.002 g), BTBAC (5.77 mol%), HCl (20.2%, 40 mL), 120 °C, 3 h.

The mass of insoluble humin formed during the reaction was also calculated. After the reaction, the humic matter was filtered under vacuum, washed with deionized water in plenty, and dried in a hot-air oven at 60 °C till constant weight was obtained. In general, less amount of humic matter was isolated from reactions using BTBAC compared to the control (no BTBAC) reactions **(Table 4.1)**. The observation indirectly supports the higher yield of LA in reactions using BTBAC as the SAA.

Table 4.1 Humin formation during the production of LA from carbohydrates

S/N	Substrate	Humin (g) (With BTBAC)	Humin (g) (No BTBAC)
1	Glucose	0.202	0.260
2	Fructose	0.251	0.312
3	Sucrose	0.220	0.263
4	Starch	0.204	0.242
5	Cellulose	0.221	0.262

Reaction conditions: Substrate (2.002 g), BTBAC (5.77 mol%), HCl (20.2%, 40 mL), 120 °C, 3 h.

4.5 CONCLUSION

A one-pot production of LA from biomass-derived carbohydrates has been achieved in 20.2% aqueous hydrochloric acid within a batch-type reactor. The reactions provided good isolated yields of LA even at high substrate loading (10 wt%) at relatively mild reaction conditions (120 °C, 3 h). The yield of LA improved noticeably by adding using an SAA as an additive. BTBAC was found to be the most effective SAA that gave 8-17% more yield of LA compared to that in the control reactions from all the carbohydrates examined. Both LA and BTBAC were isolated from the aqueous reaction mixture by distilling out aqueous hydrochloric acid or by solvent-solvent extraction.

CHAPTER 5

HIGH-YIELDING SYNTHESIS OF 5-(ALKOXYMETHYL)FURFURALS FROM BIOMASS-DERIVED 5-(HALOMETHYL)FURFURAL (X=Cl, Br)

Abstract

In this chapter, a series of 5-(alkoxymethyl)furfurals (AMFs) has been synthesized in excellent isolated yields (>90%) by reacting biomass-derived CMF or BMF with monohydric alkyl alcohols. For alcohols with smaller alkyl chain length (C1-C4), no base additive was used, and the AMFs were obtained in excellent isolated yield without requiring chromatographic purification. Although higher primary alcohols like 1-pentanol and 1-hexanol and secondary alcohol like 2-propanol, the use of N,N-diisopropylethylamine (DIPEA) as a base additive afforded the corresponding AMFs in excellent isolated yields.

5.1 INTRODUCTION

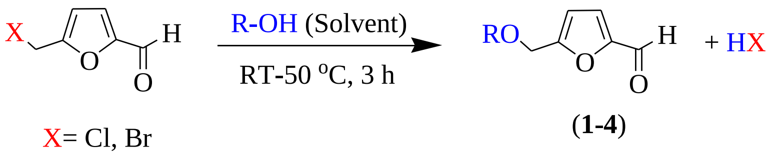
More than half of a barrel of crude oil is used as fuels in the energy and transportation sectors (Lu et al. 2007). With increasing volatility in the petroleum market, greater consciousness among the citizens, and stricter environmental regulations, the interests in renewable and green fuels have gained attraction (Climent et al. 2014, Kunkes et al. 2008). The drive towards ultra-low sulfur and cleaner-burning fuels led to the development of various oxygenated fuel additives (Kesieme et al. 2019, Verma et al. 2019). The fuel additives ensure more complete combustion, improve lubricity, and increase the octane ratings (Khan et al. 2015). 5-(Alkoxymethyl)furfural (AMF) is an interesting class of compound synthesized from the biomass-derived hexose sugars, and carbohydrates with potential applications as novel fuel oxygenate (Balakrishnan et al. 2012, Climent et al. 2014, Gruter et al. 2014, Imhof et al. 2009). AMF is produced by the etherification of HMF with alkyl alcohols. Both HMF and small-chain monohydric alcohols (e.g., ethanol, butanol) are sourced from biomass and are renewable (Alipour et al. 2017). 5-(Ethoxymethyl)furfural (EMF) is a potential biofuel candidate with an energy density of 8.7 kWh L^{-1} that is higher than ethanol (6.1 kWh L^{-1}) and comparable to gasoline (8.8 kWh L^{-1}) and diesel fuel (9.7 kWh L^{-1}) (Gruter 2009). Direct synthesis of EMF has been attempted by acid-catalyzed ethanolysis of sugars like fructose and glucose, carbohydrates like starch and cellulose, and also from lignocellulosic biomass (Alam et al. 2012, Dai et al. 2019, Morales et al. 2017, Yang et al. 2012). The reaction is believed to proceed through the intermediary of HMF. Although the above-mentioned strategy is attractive as a ‘one-pot’ production of EMF, the yield and selectivity of the reactions are generally poor (Li et al. 2016). Besides, the relatively harsh conditions required for the reaction favor side reactions such as the formation of diethyl ether from ethanol and decomposition of HMF and EMF into humin. HMF has also been used as a feedstock for the preparation of EMF (Liu et al. 2013, Wang et al. 2013). In a two-step strategy, HMF is first produced by acid-catalyzed dehydration of sugars and carbohydrates and then subjected to acid-catalyzed etherification reaction in ethanol. Although good yield and selectivity of EMF have been reported, the reaction generally requires high temperature and long reaction time and often ends up with a mixture of ethers and acetals (Lanzafame et al. 2011). In addition, the commercial viability of this process relies heavily on the economics of producing HMF. The production of HMF from biomass is still plagued with issues like scalability and efficient isolation of HMF from the hydrophilic reaction media (Iris et al. 2017, Van Putten et al. 2013). In this regard, hydrophobic analogs of HMF, such as CMF and BMF, have been produced in good isolated yields directly from biomass, and their isolation from the reaction media is relatively straightforward (Kumari et al. 2011, Mascal et al. 2008, 2009). CMF has been shown to participate virtually in all derivative chemistries of HMF (Brasholz et al. 2011, Gao et al. 2013, Laugel et al. 2014, Mascal et al. 2011, Mascal et al. 2014). Interestingly, alcohols can nucleophilically substitute the halogen atom in CMF and BMF, and unlike HMF, the process does not require any acid catalyst. The reaction of an alcohol with CMF and BMF produces one mole of HCl and HBr, respectively, which can potentially be recycled to produce more of the furanic precursors. Although high yields of EMF were reported starting from CMF and BMF, the formation of ethyl levulinate could not be avoided entirely during the work-up and purification processes. The release of HCl (or HBr) triggers the ring-opening of AMF into alkyl levulinates. In this regard, the use of an equivalent of the base during the reaction has been found to minimize or stop the formation of alkyl levulinates (Viil et al. 2014). However, the acid is converted into a salt, a process that introduces a waste stream and increases the cost of EMF as a biofuel. In this work, we have produced AMFs **1**–**7** (**Scheme 1**) in excellent isolated yields by reacting CMF and BMF with dry alcohols. The reactions were optimized on temperature, the ratio of reagents, and reaction time. In the case of AMFs (**1**–**4**), the reactions completed within 3 h at slightly elevated temperatures. A modified work-up procedure was adopted where the reaction mixture was first diluted in cold water and the product extracted in an organic solvent like chloroform. The process was found to minimize the ring-opening reaction significantly compared to the reported strategy of removing excess alcohol first by vacuum distillation. In general, alcohols with an increasing alkyl chain were found to be less reactive in AMF formation. Therefore, in the case of AMFs (**5**–**7**), the reaction had to be performed using nearly an equivalent amount of *N*,*N*-diisopropylethylamine (DIPEA) as a non-nucleophilic organic base. It may be reasoned that the possibility of losing the acid as salt may be tolerated since these AMFs would likely be used for low-volume but high-value applications. Besides, the process allows using only slight excess high-boiling alcohols, thereby simplifying the isolation and purification of AMFs. Excellent isolated yields of **5**–**7** were obtained under relatively mild reaction conditions.

5.2 EXPERIMENTAL SECTION

5.2.1 Materials

CMF and BMF were prepared and purified using a literature procedure (Mascal et al. 2008), and their purity confirmed by ^{1}H-NMR spectroscopy. Methanol (99.5%) was purchased from Fischer Scientific. Ethanol (99%), 1-propanol (99.5%), 1-butanol (99%), and 2-propanol (98%) were purchased from Loba Chemie. Chloroform (98%), 1-pentanol (99%), and 1-hexanol (99%) were purchased from Avra synthesis Pvt. Ltd. Calcium carbonate (99%), Potassium carbonate, and N,N-Diisopropylethylamine (99%) was purchased from Spectrochem. The alcohols were used after overnight drying over pre-activated molecular sieves (4 Å). All other chemicals were used as received without further purification.

5.2.2 METHOD A: Typical procedure for the synthesis of AMF (1-4)

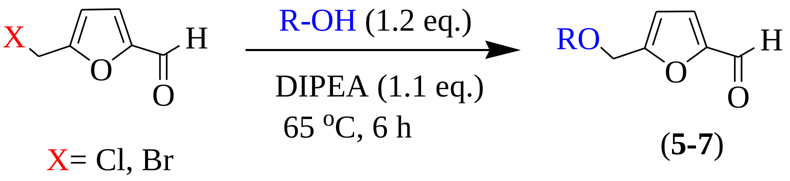


R= methyl (MMF, **1**), R= ethyl (EMF, **2**), R= 1-propyl (PrMF, **3**), R=1-butyl (BuMF, **4**)

Scheme 5.1 Preparation of AMFs from CMF and BMF using alcohol as a solvent with no base additive.

CMF (0.500 g, 3.46 mmol) and a 1-butanol (10 mL) were charged into a 50 mL round-bottom flask and fitted with a water-cooled condenser. The solution was placed in a pre-heated oil-bath (50 °C) and magnetically stirred continuously during the reaction. The reaction was monitored by TLC for the consumption of CMF. After the reaction, the mixture was cooled down to RT and diluted in ice-cold water (10 mL). The mixture was extracted with chloroform (3×10 mL). The chloroform layers were combined, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure to yield a light brown liquid. Although the ^{1}H-NMR spectrum of the crude product was found to be of high purity, it was chromatographed (Silica gel, $CHCl_3$). Evaporation of solvent provided BuMF, **4** as a yellow liquid (0.604 g, 96%).

5.2.3 METHOD B: Typical procedure for the synthesis of AMF (5-7)



R= 1-pentyl (PeMF, **5**), R= 1-hexyl (HeMF, **6**), R= 2-propyl (IpMF, **7**)

Scheme 5.2 Preparation of AMFs from CMF and BMF using a slight excess of alcohol and an equivalent of DIPEA as a base.

CMF (0.502 g, 3.46 mmol) and a 1-pentanol (0.367 g, 4.154 mmol, 1.2 eq.) were charged into a round-bottomed flask (25 mL) and fitted with a water-cooled condenser. The solution was placed in a pre-heated oil-bath (65 °C) and magnetically stirred continuously for 6 h. The reaction was monitored by TLC for the consumption of CMF. After reaction, the reaction mixture was cooled down to RT and diluted in ice-cold water (10 mL). The mixture was extracted with chloroform (3×10 mL). The chloroform layers were combined, dried over anhydrous sodium sulfate, and evaporated under reduced pressure to yield a brown liquid. The crude product was chromatographed (Silica gel, $CHCl_3$). Evaporation of solvent provided PeMF, **5** as a light-yellow oil (0.633 g, 93%).

5.3 CHARACTERIZATION OF SYNTHESIZED COMPOUNDS

The synthesized AMFs were further confirmed by FTIR, ^{1}H-NMR, and ^{13}C-NMR spectroscopic analysis, as mentioned in **Section 3.3** of CHAPTER 3.

5.3.1 FTIR, ^{1}H-NMR, and ^{13}C-NMR spectra of 5-(methoxymethyl)furfural (MMF, 1).

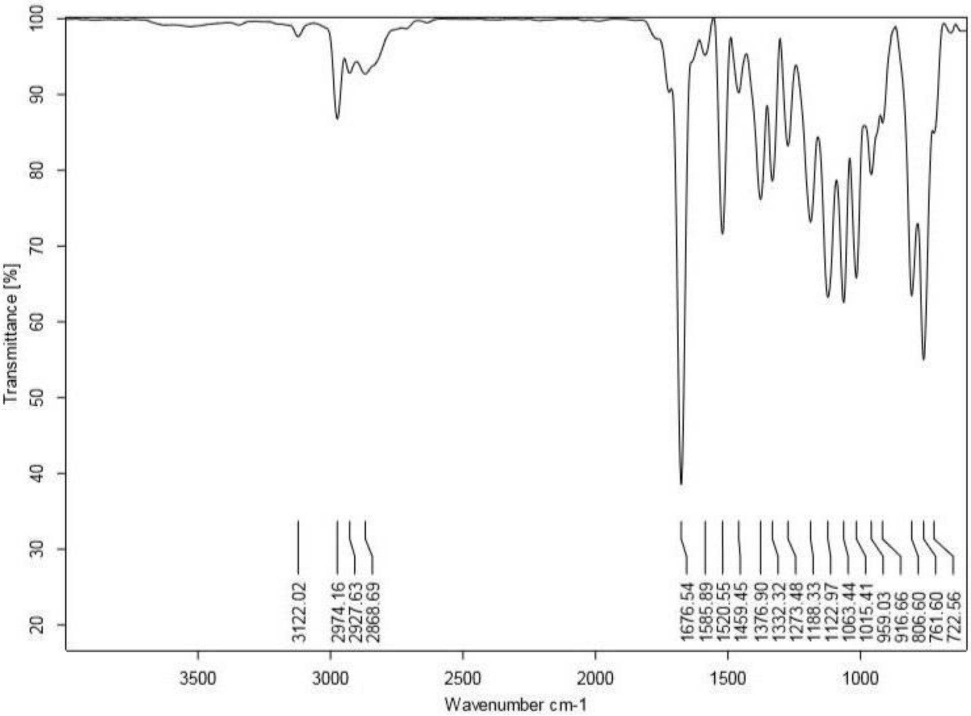


Figure 5.1 The FTIR spectrum of MMF.

The peak at 3122 cm^{-1} can be attributed to the =C-H stretch in the furan ring of MMF. The peaks around 2868-2974 cm^{-1} show the stretching vibrations of the methylene ($-CH_2$) and methyl ($-CH_3$) groups (symmetric and antisymmetric). The doublet for –C-H in the aldehyde has coincided in aliphatic –CH stretching frequency. The strong peak at 1676 cm^{-1} is due to the –C=O stretching frequency of the aldehyde. The peaks around 1000-1200 cm^{-1} show the stretching vibrations of –C-O bond.

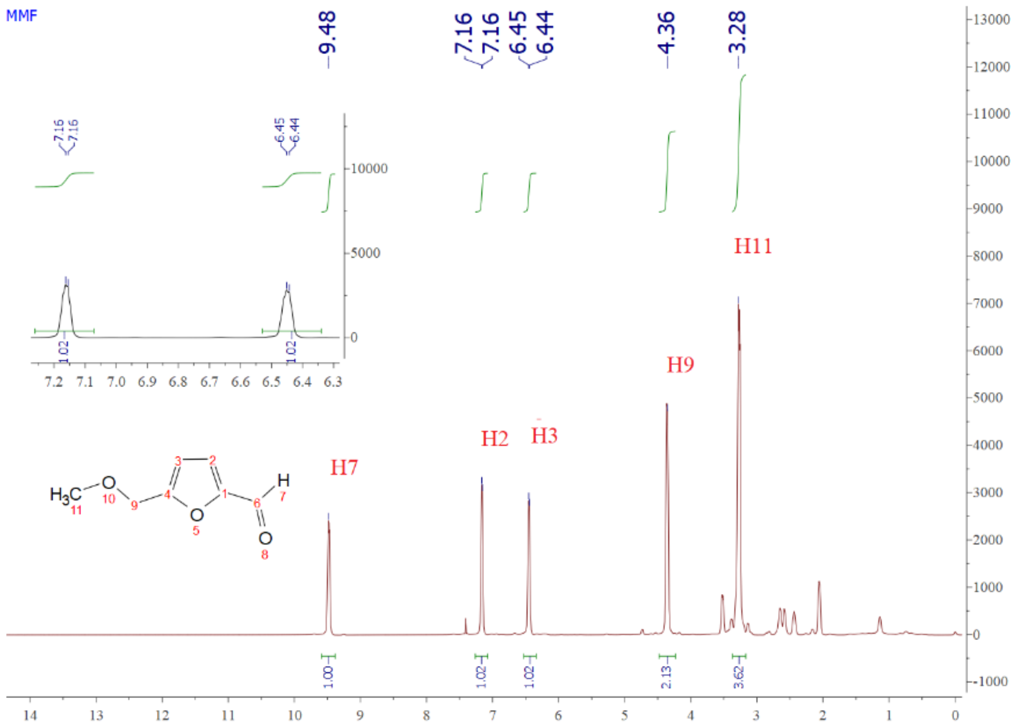


Figure 5.2 The ^{1}H-NMR spectrum of MMF.

The ^{1}H-NMR spectrum of isolated MMF shows a singlet (1H) at 9.4 ppm due to the aldehyde proton. Two doublets at 7.1 ppm and 6.4 ppm (J=3.2 Hz) (1H each) are due to the furanic protons coupling with each other. The 2H singlet at 4.3 ppm is due to the CH_2 group. The 3H singlet at 3.2 ppm is due to protons of methoxy ($-OCH_3$) group.

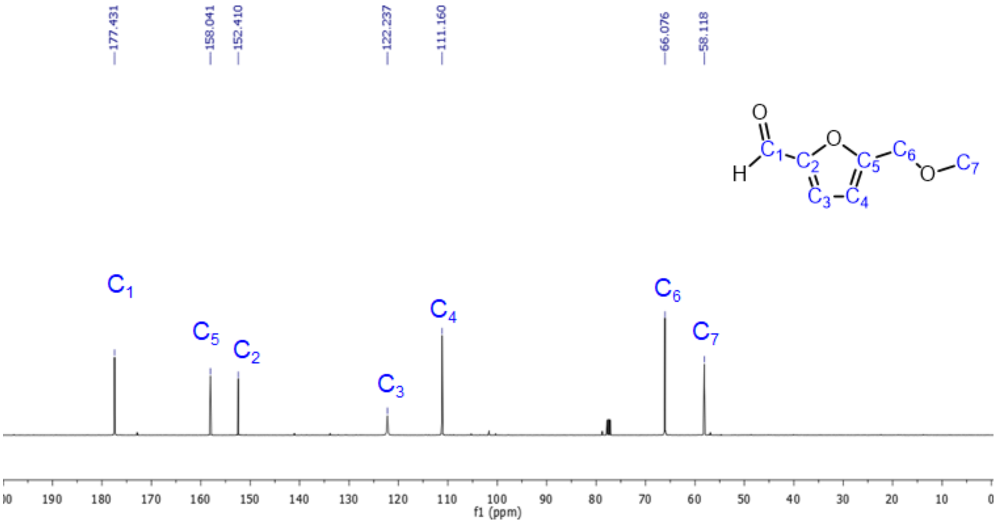


Figure 5.3 The ^{13}C-NMR spectrum of MMF.

The ^{13}C-NMR spectrum of MMF shows a peak at 177.4 ppm due to the aldehyde carbon (C=O), the peaks at 111.1 ppm and 122.2 ppm correspond to the furanic carbons at the 3rd and 4th positions. The two peaks at 158.0 and 152.4 are due to furanic carbons at the 2nd and 5th positions. The peak at 66.0 ppm is due to the methylene carbon. The peak at 58.1 ppm corresponds to the methoxy (–OCH_3) group.

5.3.2 FTIR, ^{1}H-NMR and ^{13}C-NMR spectra of 5-(ethoxymethyl)furfural (EMF, 2)

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 9.55 (1H, s), 7.15 (1H, d, 3.6 Hz), 6.46 (1H, d, 3.6 Hz), 4.47 (2H, s), 3.52 (2H, q, 7.2 Hz), 1.18 (3H, t, 7.2 Hz).^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 176.7, 157.7, 151.5, 120.9, 109.9, 65.6, 63.7, 14.0. FTIR (ATR, cm^{-1}): 3121, 1676, 1520, 1090.

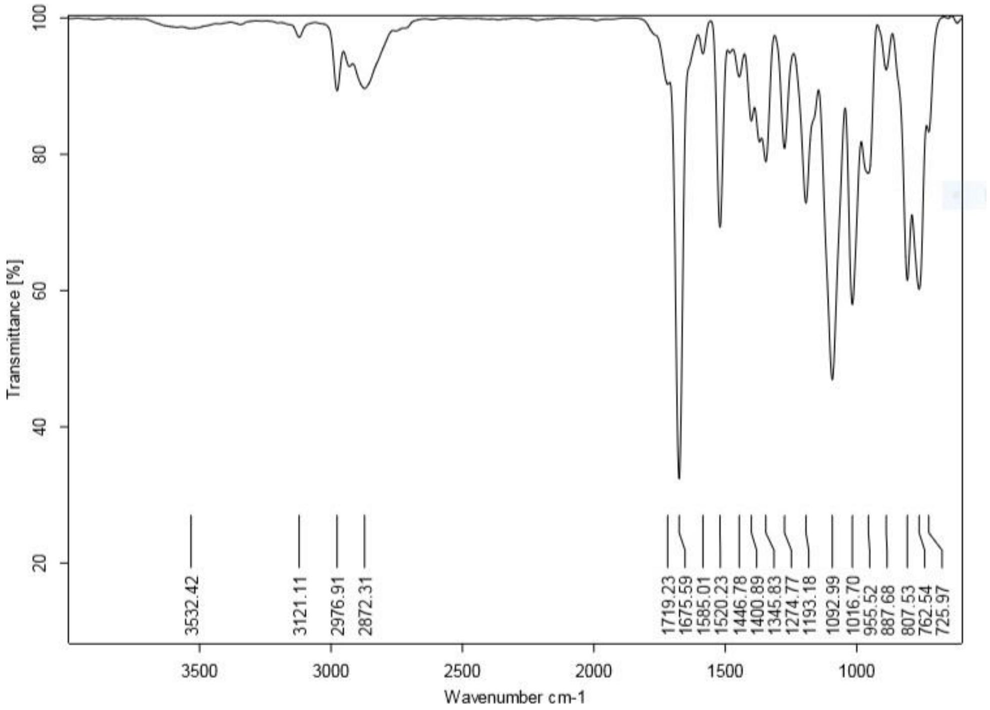


Figure 5.4 The FTIR spectrum of EMF.

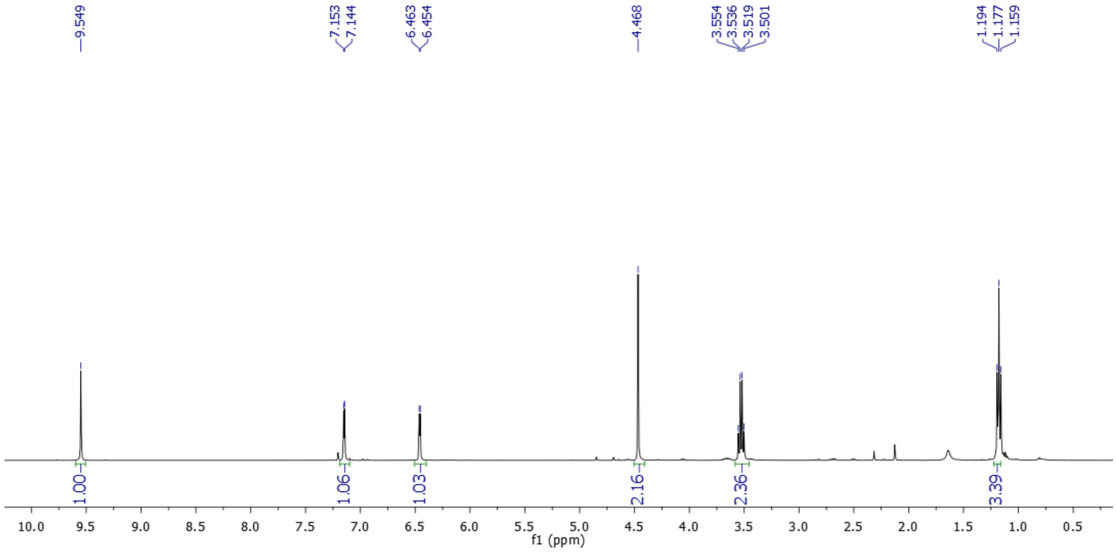


Figure 5.5 The ^{1}H-NMR spectrum of EMF.

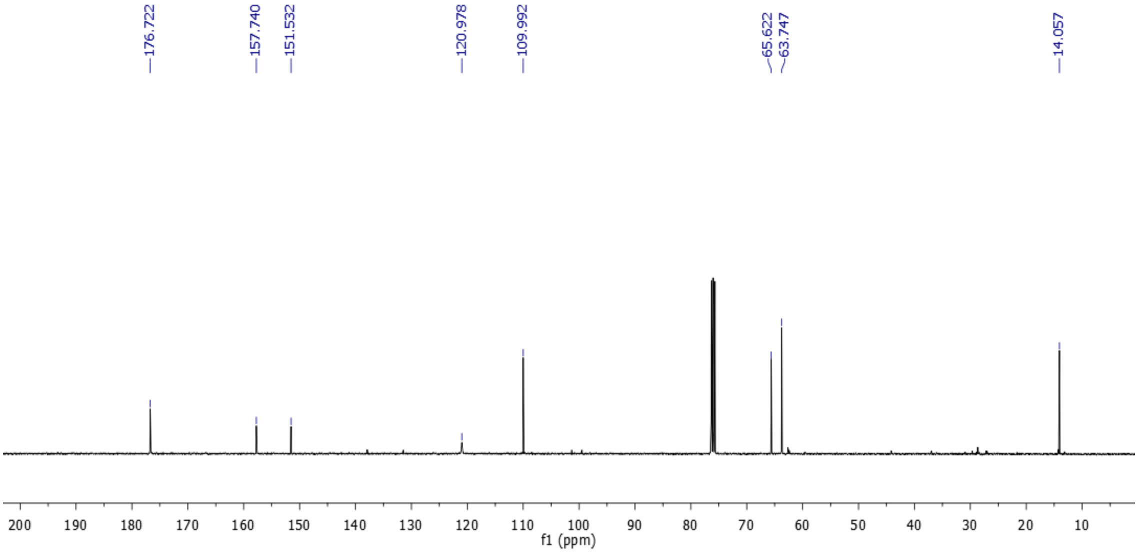


Figure 5.6 The ^{13}C-NMR spectrum of EMF.

5.3.3 FTIR, ^{1}H-NMR and ^{13}C-NMR spectra of 5-(propoxymethyl)furfural (PrMF, 3)

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 9.62 (1H, s), 7.22 (1H, d, 3.6 Hz), 6.52 (1H, d, 3.6 Hz), 4.54 (2H, s), 3.49 (2H, t, 7.2 Hz), 1.64 (2H, m), 0.93 (3H, t, 7.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 177.7, 158.9, 152.5, 122.1, 110.9, 72.9, 64.9, 22.8, 10.5. FTIR (ATR, cm^{-1}): 3121, 1677, 1520, 1092.

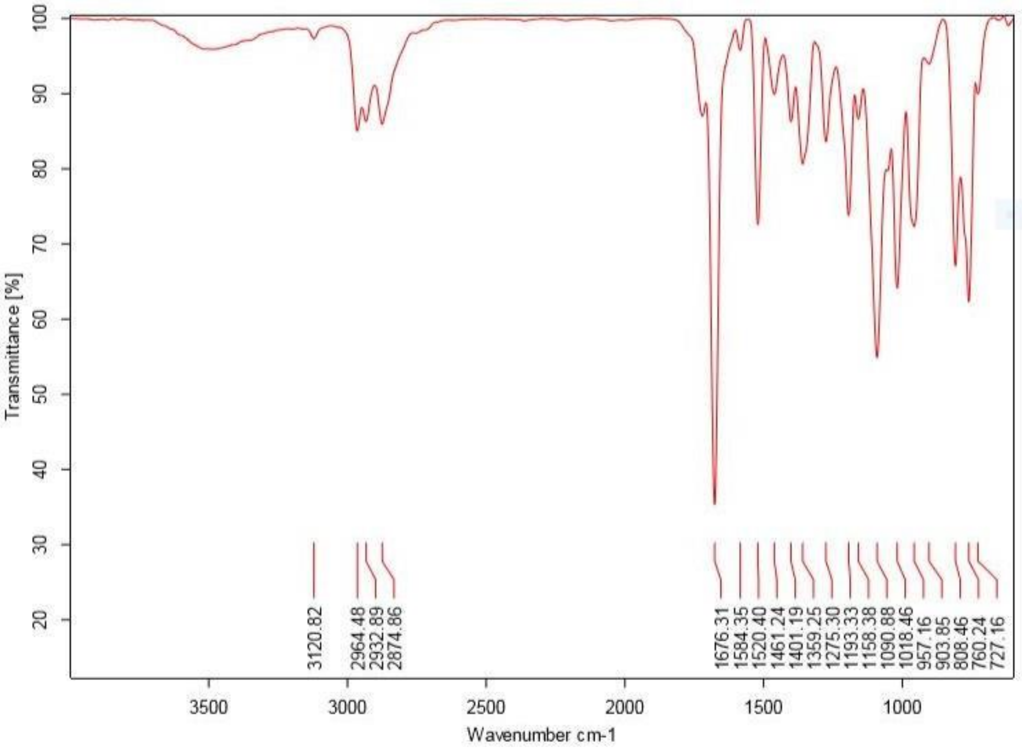


Figure 5.7 The FTIR spectrum of PrMF.

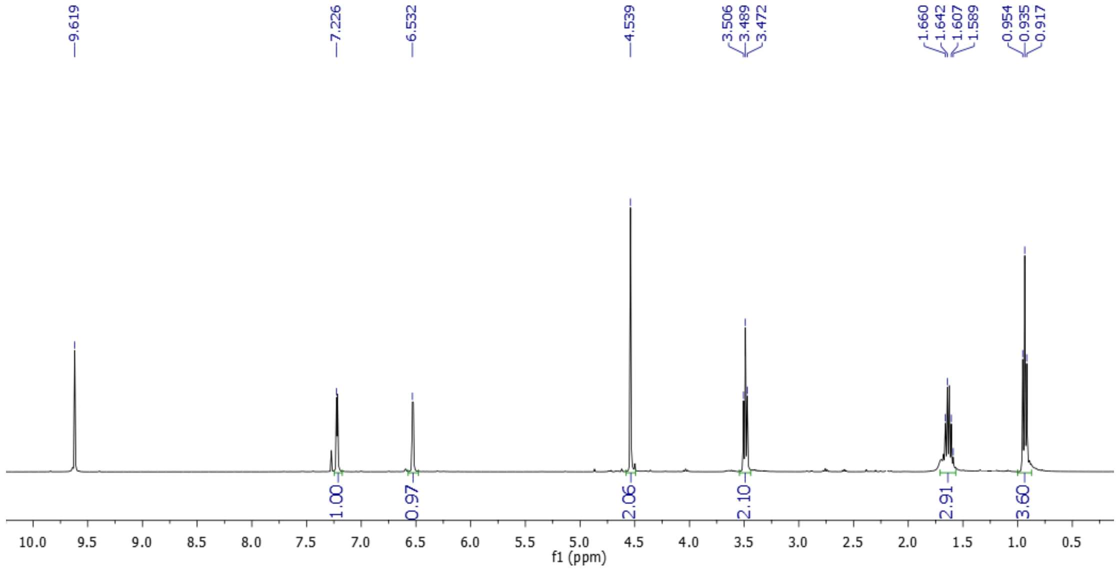


Figure 5.8 The ^{1}H-NMR spectrum of PrMF.

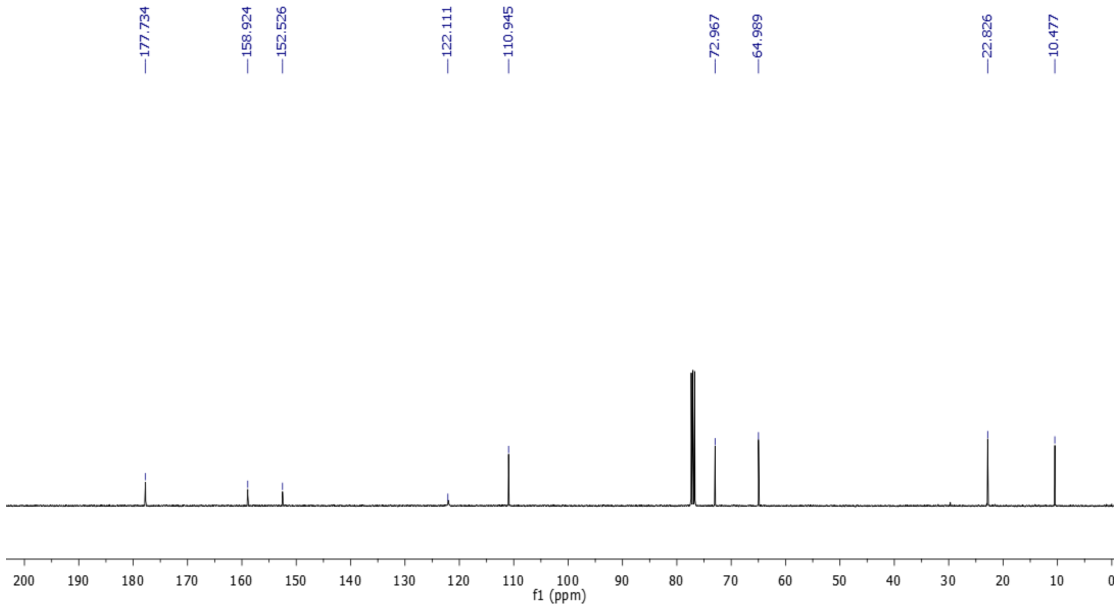


Figure 5.9 The ^{13}C-NMR spectrum of PrMF

5.3.4 FTIR, ^{1}H-NMR and ^{13}C-NMR spectra of 5-(butoxymethyl)furfural (BuMF, 4)

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 9.61 (1H, s), 7.21 (1H, d, 3.2 Hz), 6.52 (1H, d, 3.2 Hz), 4.53 (2H, s), 3.52 (2H, t, 6.4 Hz), 1.61 (2H, m), 1.35 (2H, m), 0.91 (3H, t, 6.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 177.7, 158.9, 152.5, 122.0, 110.9, 71.1, 65.0, 31.6, 19.2, 13.8. FTIR (ATR, cm^{-1}): 3120, 1677, 1520, 1092.

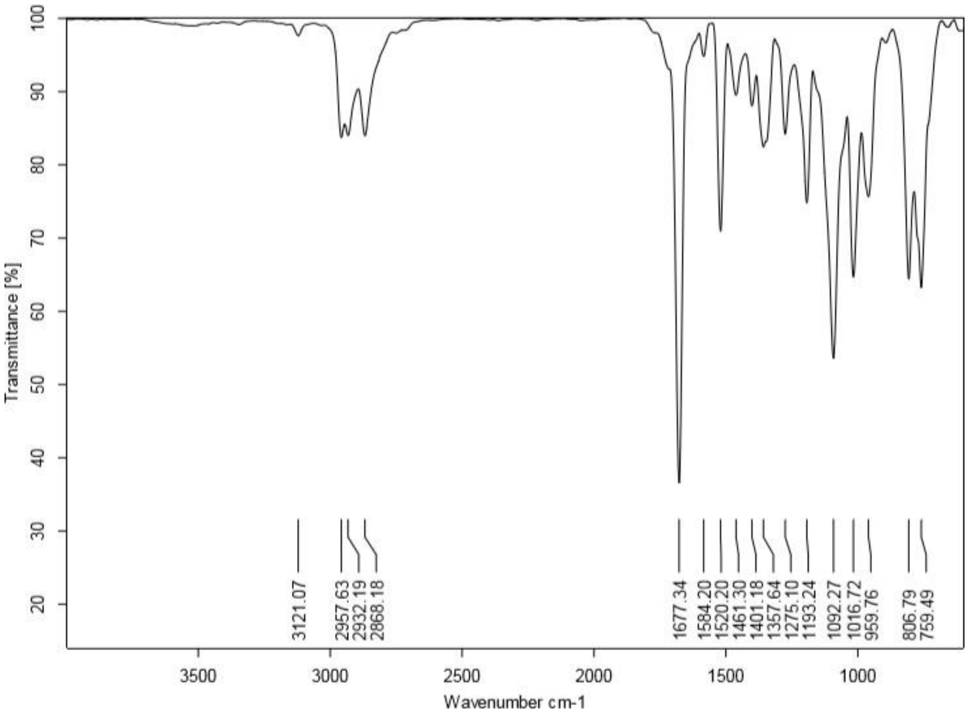


Figure 5.10 The FTIR spectrum of BuMF.

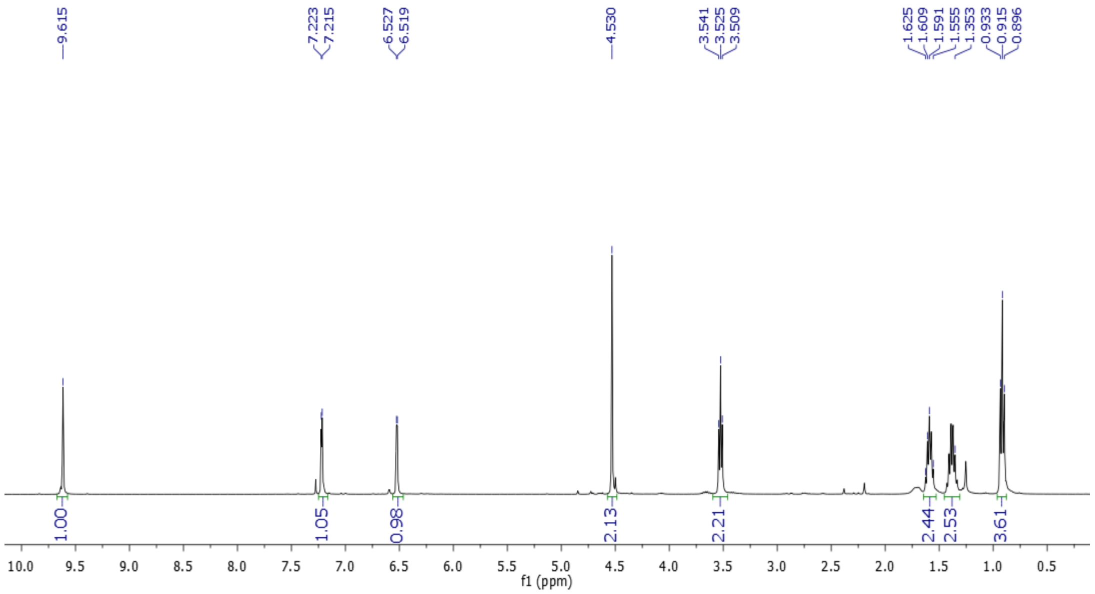


Figure 5.11 The ^{1}H-NMR spectrum of BuMF.

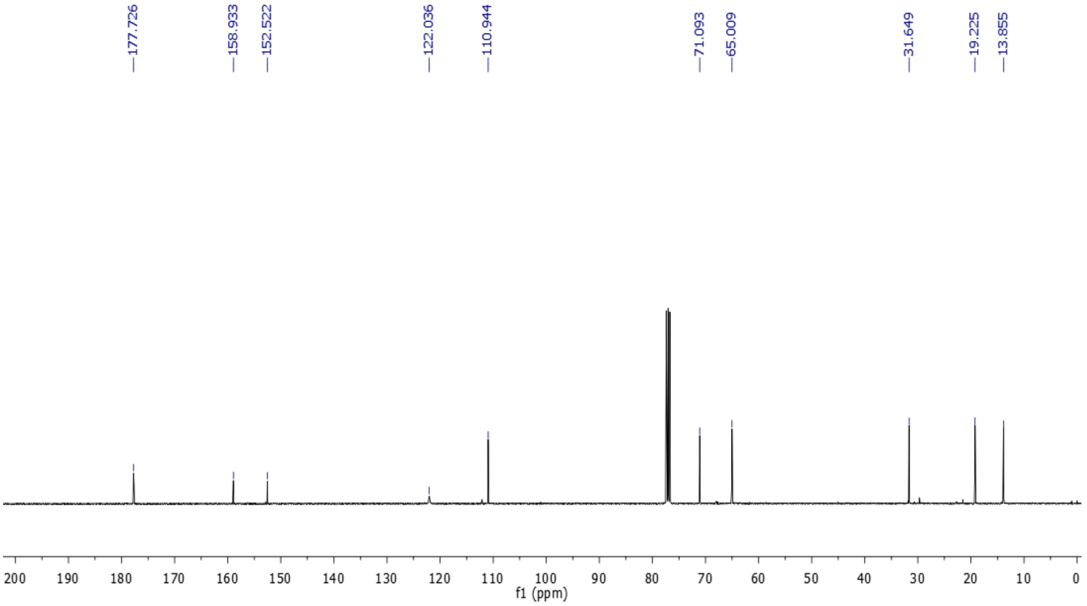


Figure 5.12 ^{13}C-NMR spectrum of BuMF.

5.3.5 FTIR, ^{1}H-NMR and ^{13}C-NMR spectra of 5-(pentyloxymethyl)furfural (PeMF, 5)

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 9.61 (1H, s), 7.21 (1H, d, 3.6 Hz), 6.52 (1H, d, 3.6 Hz), 4.53 (2H, s), 3.51 (2H, t), 1.61 (2H, m), 1.31 (4H, m), 0.89 (3H, t). ^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 177.7, 158.9, 152.5, 121.9, 110.9, 71.4, 65.0, 29.3, 28.2, 22.5, 14.0. FTIR (ATR, cm^{-1}): 3117, 1678, 1558, 1093.

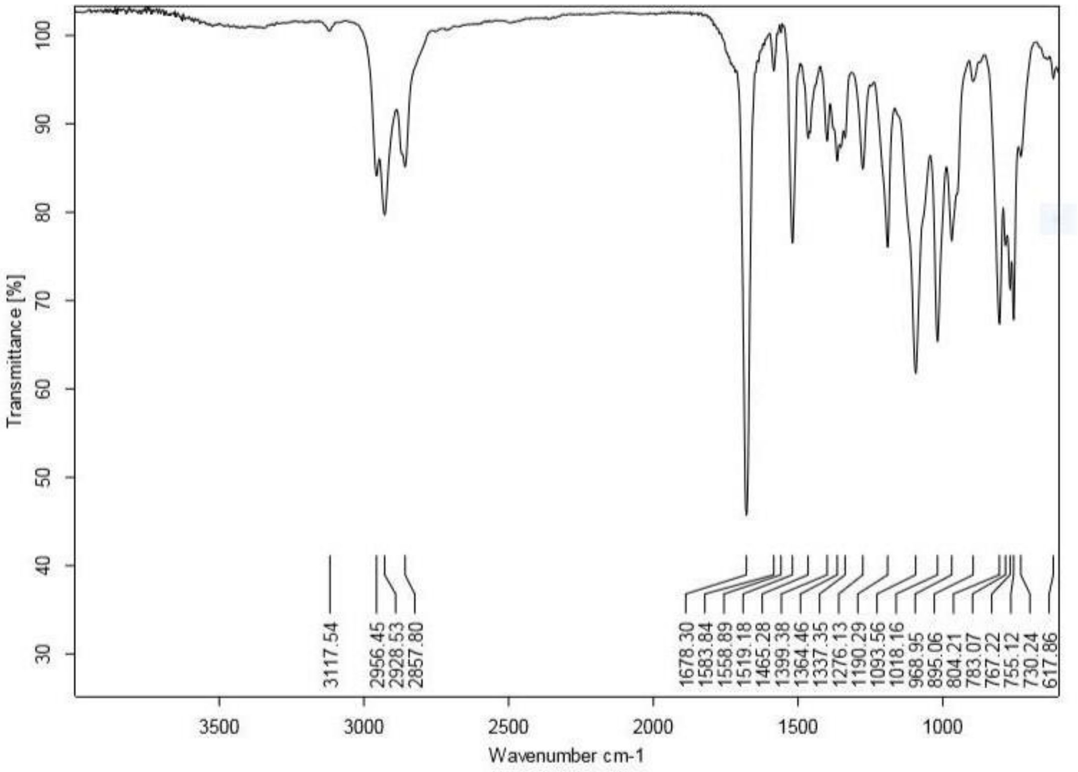


Figure 5.13 The FTIR spectrum of PeMF.

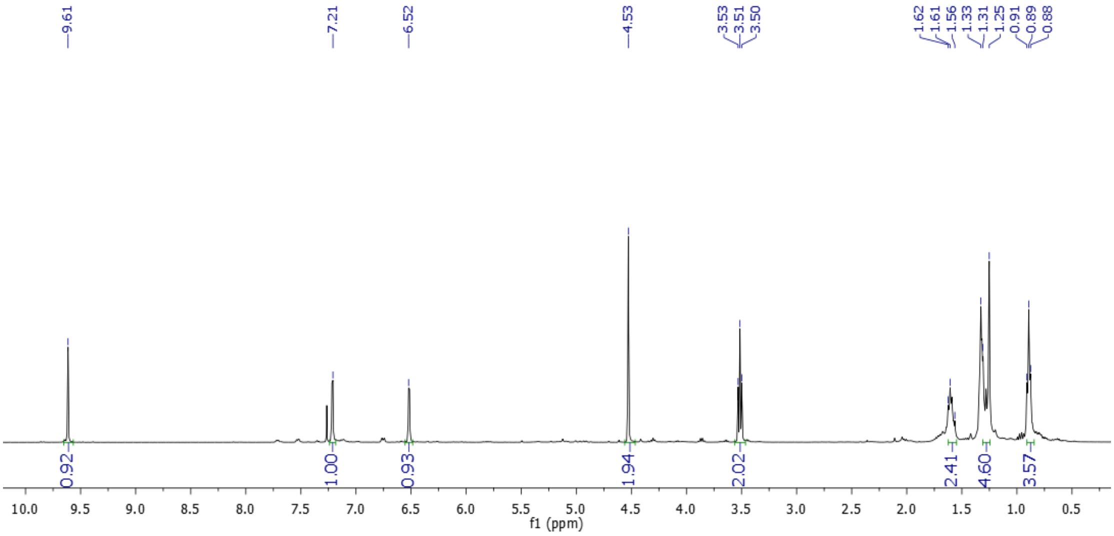


Figure 5.14 The ^{1}H-NMR spectrum of PeMF.

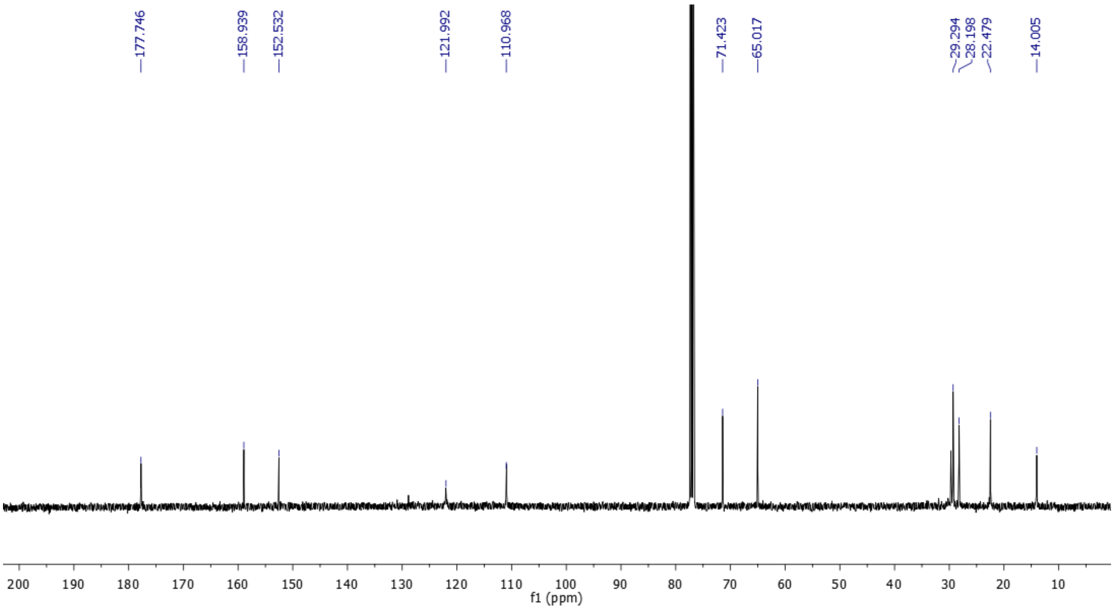


Figure 5.15 The ^{13}C-NMR spectrum of PeMF.

5.3.6 FTIR, ^{1}H-NMR and ^{13}C-NMR spectra of 5-(hexyloxymethyl)furfural (HeMF, 6)

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 9.54 (1H, s), 7.15 (1H, d, 3.2 Hz), 6.45 (1H, d, 3.2 Hz), 4.48 (2H, s), 3.57 (2H, t, 7.2 Hz), 1.49 (2H, m), 1.24 (6H, m), 0.82 (3H, m). ^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 177.7, 158.8, 152.4, 122.1, 110.9, 71.3, 64.9, 31.5, 29.5, 25.6, 22.5, 13.9. FTIR (ATR, cm^{-1}): 3119, 1684, 1520, 1062.

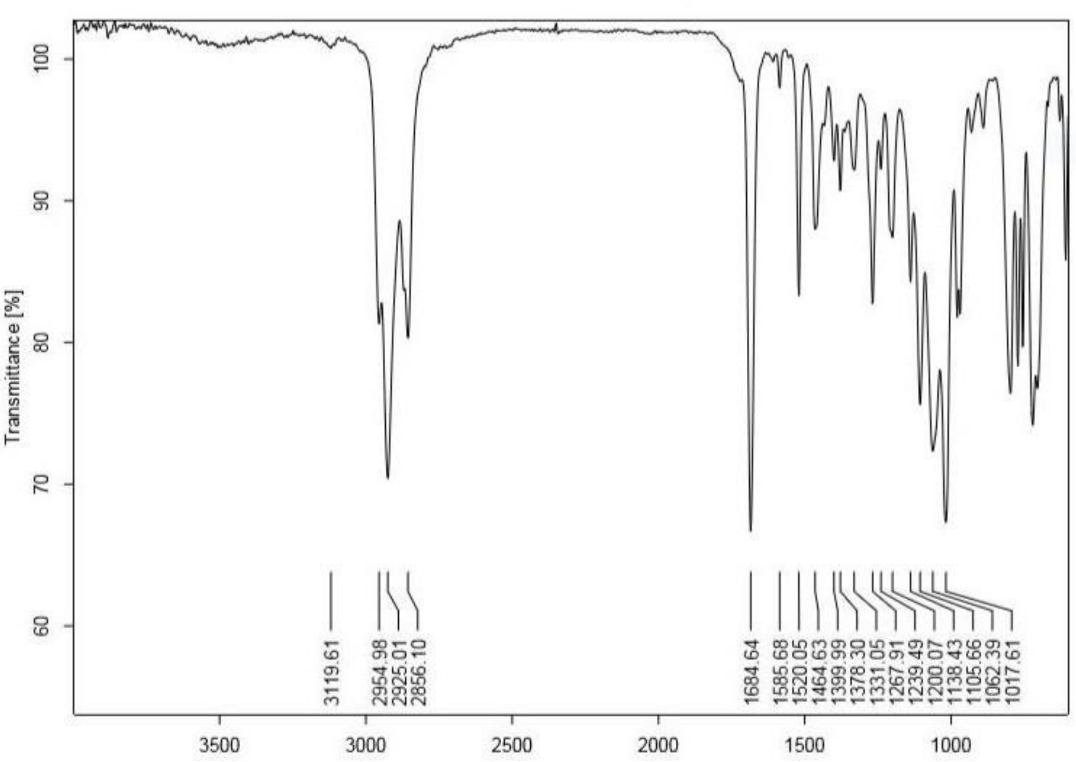


Figure 5.16 The FTIR spectrum of HeMF.

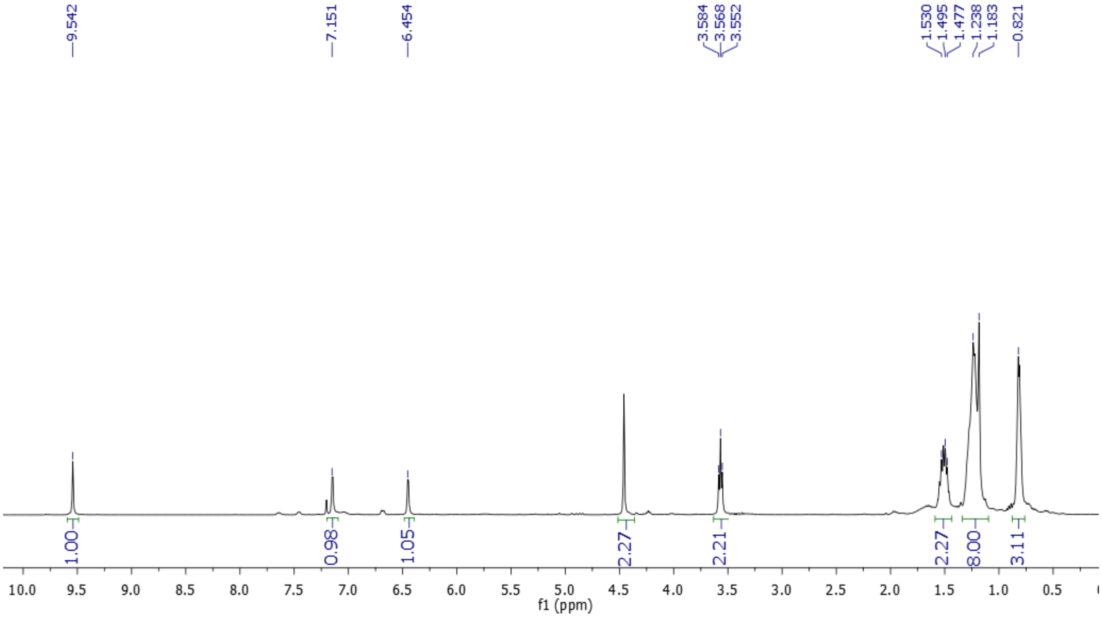


Figure 5.17 The ^{1}H-NMR spectrum of HeMF.

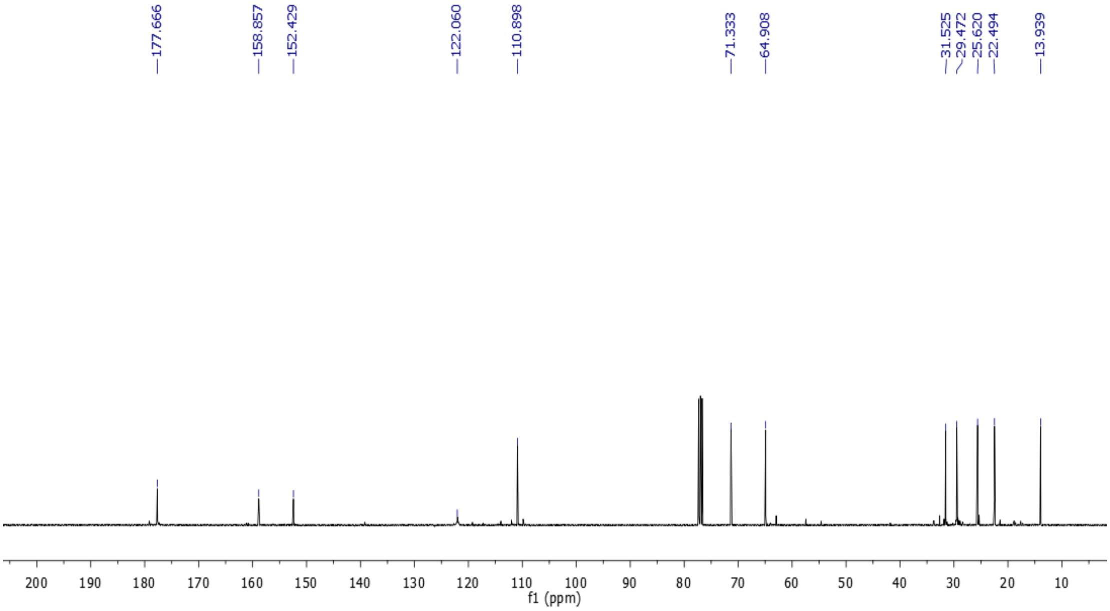


Figure 5.18 The ^{13}C-NMR spectrum of HeMF.

5.3.7 FTIR, ^{1}H-NMR and ^{13}C-NMR spectra of 5-(isopropoxymethyl)furfural (IpMF, 7)

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 9.52 (1H, s), 7.15 (1H, d, 3.2 Hz), 6.44 (1H, d, 3,2 Hz), 4.47 (2H, s), 3.65 (1H, m), 1.13 (6H, d). ^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 176.6, 158.3, 151.4, 121.3, 109.7, 71.0, 61.4, 20.9. FTIR (ATR cm^{-1}) 3122, 1676, 1520, 1063.

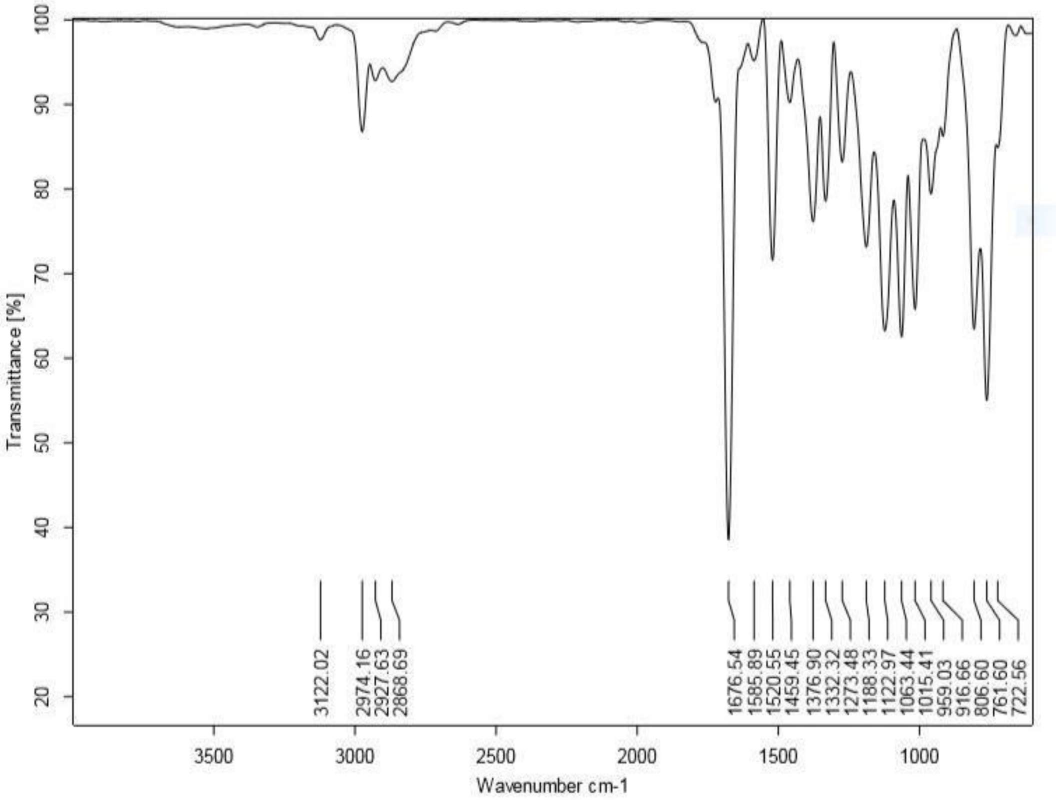


Figure 5.19 The FTIR spectrum of IpMF.

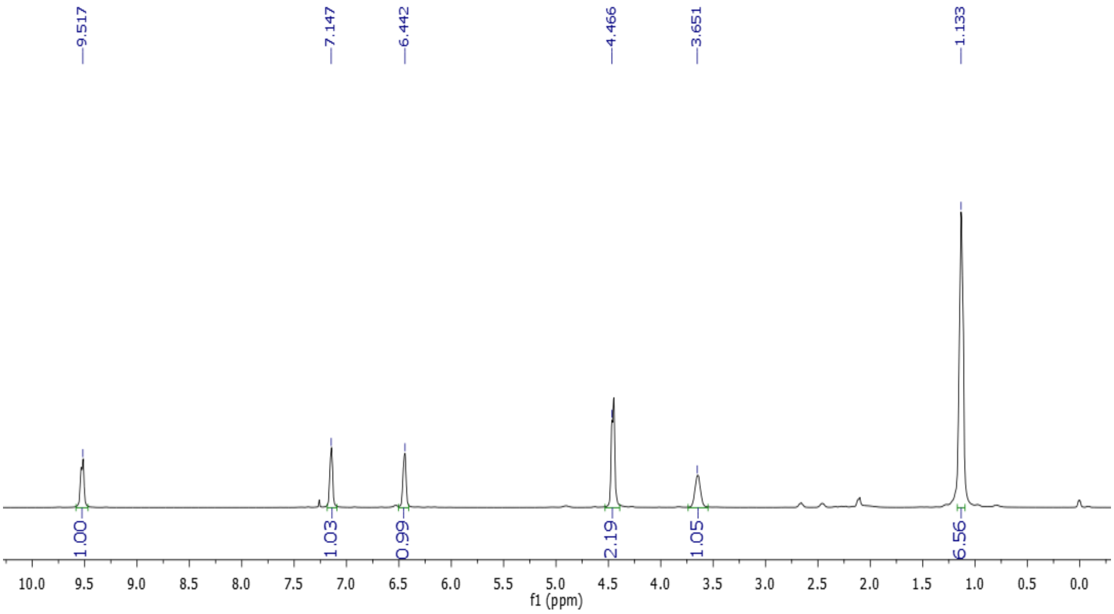


Figure 5.20 The ^{1}H-NMR spectrum of IpMF.

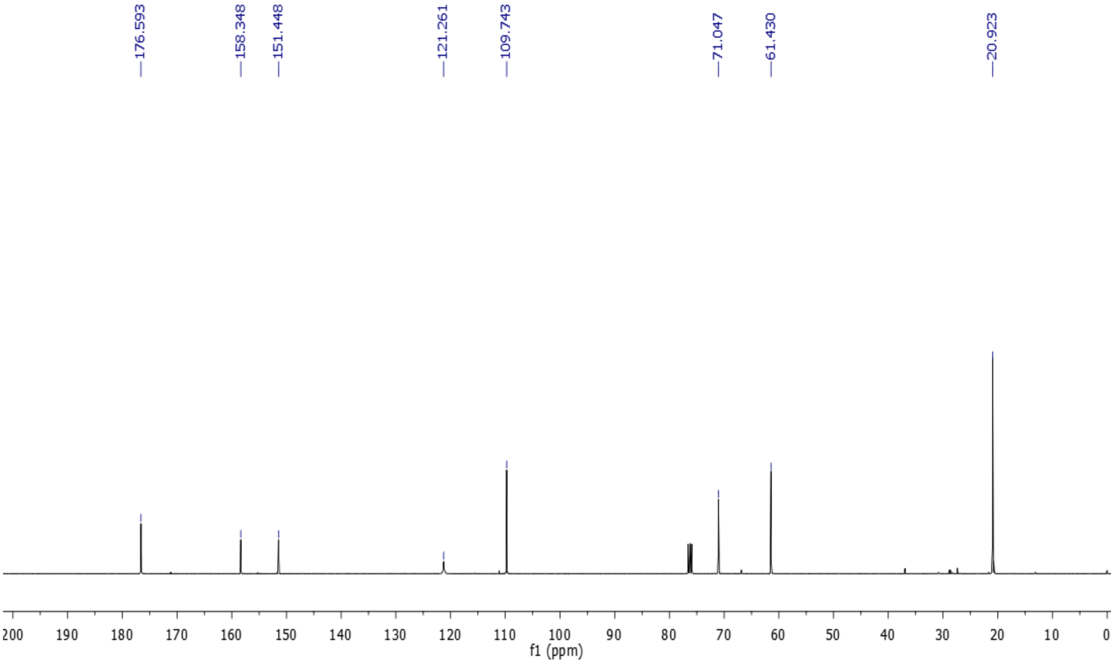


Figure 5.21 The ^{13}C-NMR spectrum of IpMF.

5.4 RESULTS AND DISCUSSION

5.4.1 Synthesis of AMF (1-4) from XMF using lower alcohols

Initially, the synthesis of EMF, **2** was attempted using a reported procedure (Mascal et al. 2009). CMF was dissolved in excess anhydrous ethanol and mechanically stirred at room temperature till complete conversion of CMF. As reported, the reaction took long time (*ca.* 8 h) to complete. When the temperature was raised slightly to 50 °C, the reaction was found to complete within 3 h. No ring-opened product (*e. g.*, ethyl levulinate) formed under this condition as confirmed by FTIR and ^{1}H-NMR spectra of the crude reaction mixture. The reaction works similarly with BMF as the substrate. When CMF or BMF was reacted with methanol as solvent, the reaction completes within 3 h even at RT to yield 5-(methoxymethyl)furfural (MMF, **1)**. The reaction was worked up following the same literature process where the excess alcohol was first removed by evaporation under vacuum. Interestingly, ethyl levulinate and some humin formed during the evaporation of alcohol as confirmed by spectroscopic analysis. This observation may be explained by the increasing concentration of dissolved HCl or HBr acid in ethanol during its evaporation that triggers the ring-opening reaction. Therefore, to avoid building-up acid concentration during work-up, the crude reaction mixture was first diluted in ice-cold water and the product extracted in chloroform to minimize the formation of ethyl levulinate and humin. Using the modified work-up procedure, EMF was obtained in 90% and 92% isolated yields starting from CMF and BMF, respectively **(Table 5.1, Entry 2)**. The same work-up procedure afforded MMF, **1** in 91% and 93% isolated yields starting from CMF and BMF, respectively **(Table 5.1, Entry 1)**. The trend of lower reactivity of alcohols with higher alkyl chain is pronounced in the case of 5-(propoxymethyl)furfural (PrMF, **3)** and 5-(butoxymethyl)furfural (BuMF, **4)**. The conversion of CMF or BMF was not complete even after overnight reaction at RT. The reaction of CMF or BMF with 1-propanol and 1-butanol requires 50 °C to complete within 3 h. Following the same work-up procedure, PrMF, **3** and BuMF, **4** were isolated in 92% and 96% isolated yields using CMF as substrate **(Table 5.1, Entry 3&4)**. BMF provided slightly better yields of AMFs when compared to CMF under comparable reaction conditions. All the reactions were performed using suitable alcohol as the solvent. When less alcohol reagent (2-5 eq.) was used, the reaction slowed down significantly and did not complete even after 6 h at 50 °C. Forcing the reaction to completion at higher temperatures led to the formation of alkyl levulinates and humin.

Table 5.1 Synthesis of AMF (**1-4**) from CMF and BMF

Entry	Substrate	Reaction conditions [a]	Product	Yield (%) [b]
1	CMF (BMF)	RT, 3 h	MMF, **1**	91 (93)
2	CMF (BMF)	50 °C, 3 h	EMF, **2**	90 (92)
3	CMF (BMF)	50 °C, 3 h	PrMF, **3**	92 (94)
4	CMF (BMF)	50 °C, 3 h	BuMF, **4**	96 (97)

[a] The reaction uses 0.5 g of the substrate and 10 mL of anhydrous alcohol; [b] The number in parenthesis is the yield from BMF. All the yields are isolated yields.

5.4.2 Synthesis of AMF (5-7) from XMF using higher alcohols

The reaction between CMF (or BMF) and higher alkyl alcohols like 1-pentanol and 1-hexanol did not complete after 6 h even at 65 °C. In an attempt to make the reaction faster, when the reaction was conducted at 80 °C, a noticeable amount of alkyl levulinates and humin formation were observed. We envisioned that a base additive would steer the reaction into completion in a reasonable time and under milder conditions by quenching the acid produced during the reaction. Both inorganic and organic bases were screened, and their effects on the yield of 5-(pentyloxymethyl)furfural (PeMF, **5)** are listed in **Table 5.2**.

Table 5.2 Effect of base additive in the synthesis of PeMF, **5**

Entry	Substrate	Reaction conditions [a]	Base additive	Yield (%) [b]
1	CMF	65 °C, 6 h	$CaCO_3$	82 (6)
2	CMF	65 °C, 6 h	K_2CO_3	86 (8)
3	CMF	65 °C, 6 h	DIPEA	94
4	CMF	65 °C, 6 h	Et_3N	60[c]

[a] The reaction uses 0.5 g of CMF, 1.2 equivalent of 1-pentanol and 1.1 equivalent of base additive [b] Isolated yields of PeMF, the number in the bracket is yield of pentyl levulinate. For **Entry 1&2**, around 0.02 g of insoluble black solid was also recovered. [c] CMF reacted with Et_3N to form a substituted product.

Initially, the reaction was performed using 1-pentanol a solvent as in the case of AMFs **1–4**. However, removal of excess 1-pentanol is tedious and energy-intensive, requiring a longer time and stronger vacuum. To optimize the reaction further, when only slight excess (*i.e.*, 1.2 equivalent) of 1-pentanol was used, the reaction worked equally well and afforded PeMF, **5** in good yields. When $CaCO_3$ and K_2CO_3 were used as a base additive, PeMF, **5** was isolated in 82% and 86% yield, respectively **(Table 5.2, Entry 1&2)**. Although the inorganic bases provided decent yields, the formation of pentyl levulinate and insoluble humin formation could not be avoided altogether. This observation can be explained by the poor solubility of inorganic bases in 1-pentanol limiting their efficiency in quenching the acids liberated during reaction. Organic amines were then chosen as the base additive working under homogeneous reaction conditions. When triethylamine was used as a base, a significant side reaction was observed where triethylamine acted as a nucleophile and substituted the chloromethyl group in CMF **(Table 5.2, Entry 4)**. *N,N*-Diisopropylethylamine (DIPEA) is a non- nucleophilic base frequently used in synthetic organic chemistry as a proton sponge. The use of an equivalent of DIPEA in the reaction medium virtually stopped the humin formation and ring-opening reaction altogether and provided PeMF, **5** in 94% isolated yield within 6 h at 65 °C. Therefore, DIPEA was chosen as the base additive of choice for the synthesis of AMFs **5–7**.

5.4.3 Effect of XMF to pentanol molar ratio on PeMF yield

The reaction was then optimized on the equivalent of 1-pentanol. The reaction works best with 1.2 equivalent of 1-pentanol with a 93% isolated yield of PeMF, **5 (Figure 5.22)**. Higher equivalents of 1-pentanol do not have a significant impact on the yield. However, lower equivalents of 1-pentanol drastically lowered the yield.

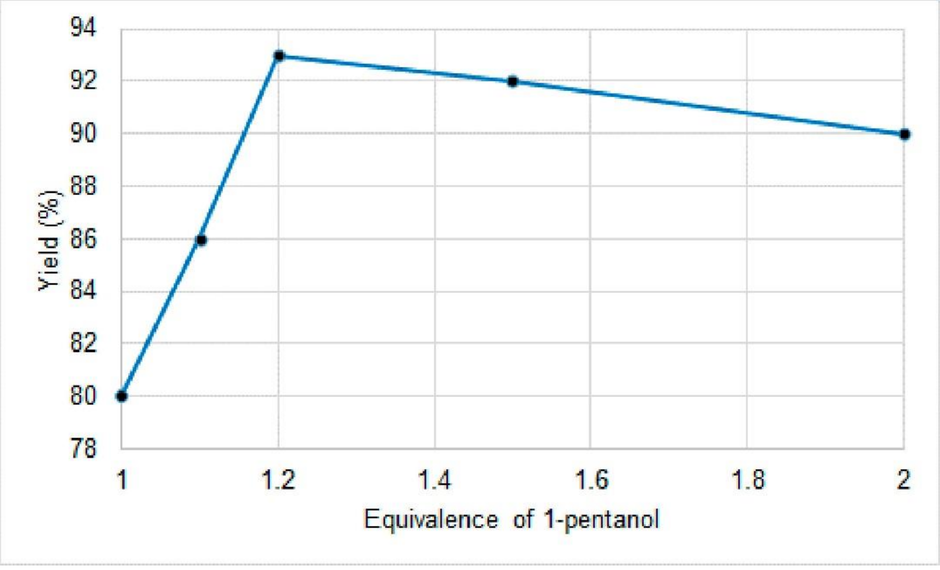


Figure 5.22 Yields of PeMF, **5** with respect to the equivalence of 1-pentanol used. **Reaction conditions:** CMF (0.5 g), 65 °C, 3 h, DIPEA (1.1 eq.), 1-pentanol.

AMFs (**5-7**) were prepared from CMF, and BMF using the optimized conditions, and their yields are tabulated in **Table 5.3**.

Table 5.3 Synthesis of AMF (**5-7**) from CMF and BMF

Entry	Substrate	Reaction conditions[a]	Product	Yield (%)[b]
1	CMF (BMF)	65 °C, 6 h	PeMF, **5**	93 (94)
2	CMF (BMF)	65 °C, 6 h	HeMF, **6**	94 (96)
3	CMF (BMF)	65 °C, 6 h	IpMF, **7**	90 (92)

[a] The reaction uses 0.5 g of the substrate and 1.2 equivalent of anhydrous alcohol in the presence of DIPEA (1.1 eq.). [b] Isolated yields. The number in parenthesis is the yield from BMF.

As observed in the case of AMFs **1–4**, BMF provided slightly better yields of AMFs **5–7** compared to CMF. For example, PeMF, **5** and 5-(hexyloxymethyl)furfural (HeMF, **6)** were obtained in 93% and 94%, respectively starting from CMF. Use of BMF as the substrate provided **5** and **6** in 94% and 96% isolated yields under identical reaction conditions **(Table 5.3**, **Entry 1&2)**. Using 2-propanol as the alcohol reagent, 5-(isopropoxymethyl)furfural (IpMF, **7**) was synthesized in 90% and 92% isolated yields from CMF and BMF, respectively.

5.5 CONCLUSION

A series of 5-(alkoxymethyl)furfurals have been synthesized in excellent isolated yields starting from biomass-derived 5-(halomethyl)furfural (X=Cl, Br). The lower alcohols (methanol to 1-butanol) were used as a solvent for the nucleophilic substitution reaction that completed within 3 h at a slightly elevated temperature. A general synthetic protocol was developed that does not require any base additive. The reactivity of higher primary alcohols and secondary alcohol was found to be less, but DIPEA was found to be an efficient organic base additive that provided AMFs in excellent yields using an only slight excess of the alcohol reagent.

CHAPTER 6

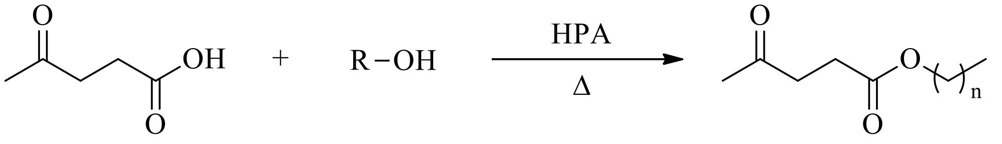
PREPARATION OF ALKYL LEVULINATES FROM BIOMASS-DERIVED FURFURYL ALCOHOL, LEVULINIC ACID, AND 5-(HALOMETHYL)FURFURAL (X=Cl, Br) USING HOMOGENEOUS AND HETEROGENEOUS CATALYSTS

Abstract

In this chapter, the synthesis of a series of ALs from biomass-derived 5-(halomethyl)furfural (X=Cl, Br), Levulinic acid, and furfuryl alcohol using both homogeneous as well as heterogeneous solid acid catalysts have been described. Keggin-type commercial heteropolyacids (HPAs) and silica-supported perchloric acid ($HClO_4$-SiO_2) *have been used as efficient solid acid catalysts for the etherification of LA as well as the alcoholysis of XMF, and furfuryl alcohol, respectively. The solvent-free, one-pot preparation afforded levulinate esters in excellent isolated yields (>90%) in a batch-type glass pressure reactor under moderate reaction conditions.*

6.1 INTRODUCTION

Alkyl levulinates (ALs) are important biorenewable compounds with commercial applications as green solvent, fuel oxygenate, renewable polymers, surfactants, and plasticizers (Adeleye et al. 2019, Démolis et al. 2014, Li et al. 2018, Yang et al. 2018). In addition, they serve as chemical intermediates for the synthesis of other valuable products such as γ-valerolactone and 2-methyltetrahydrofuran (Alonso et al. 2013, Yan et al. 2017). Ethyl levulinate (EL) has been of particular interest as a diesel-additive that enhances the lubricity of ultra-low-sulfur diesel (Joshi et al. 2011, Wang et al. 2012). The addition of EL reduces the emission of CO and particulate matter and improves the cold-flow properties of bio-diesel (Joshi et al. 2011, Wang et al. 2012). At present, the ALs are generally produced by the Fischer esterification of LA or alcoholysis of HMF and furfuryl alcohol in the presence of a suitable acid catalyst (Ahmad et al. 2016, Fernandes et al. 2012, Flannelly et al. 2015, Yang et al. 2019, Zhao et al. 2019). The synthesis of EL has also been achieved from LA-derived angelica lactone (Al-Shaal et al. 2015). One-pot preparation of ALs can also be achieved by treating carbohydrates and cellulosic biomass with alcohols in the presence of a suitable acid catalyst (Peng et al. 2011, Zhao et al. 2015). Although ALs have been produced in good selectivity and yield from HMF or LA, the commercial viability of the process relies heavily on the feasibility of producing HMF or LA from the inexpensive biomass-based feedstock (Arslan et al. 2014). Although the high yield of HMF and LA has been reported from simple sugars, the same from untreated biomass is relatively rare and often requires special reaction conditions that negatively affect scalability and process economics (Menegazzo et al. 2018). One-pot preparation of AL from carbohydrates often suffers from low selectivity and yield and leads to the dehydration of alcohol to ether (Rao et al. 2018). The present study demonstrates two different synthetic protocols for the preparation of ALs from biomass-derived LA, XMF (X=Cl, Br), and furfuryl alcohol. The Fischer esterification of LA with monohydric alkyl alcohols typically uses an acid catalyst of some sort. Although significant research has been devoted in developing suitable catalysts for this transformation, there is a constant search for efficient, recyclable, and eco-friendly catalysts that allows the reaction to proceed under mild condition and produce the product in high yield. In this regard, HPAs are well-structured metal-oxygen clusters with strong Brønsted acidity, high thermal stability, tunable solubility, less corrosivity, and low toxicity (Katsoulis 1998, Mal et al. 2013). HPAs are miscible in polar solvents like methanol but immiscible in non-polar organic solvents like diethyl ether. Therefore, the solubility characteristics of HPA can be exploited where it can be used as a homogeneous catalyst in the alcoholic reaction media but made heterogeneous after reaction by precipitating it in a non-polar solvent (Wang et al. 2015). In the present work, commercially-available Keggin-type solid HPAs, namely, phosphotungstic acid (PTA), phosphomolybdic acid (PMA), and silicotungstic acid (SMA) have been examined as catalysts for the esterification of LA with monohydric alkyl alcohols (C1-C6) under homogeneous condition **(Scheme 6.1)**.

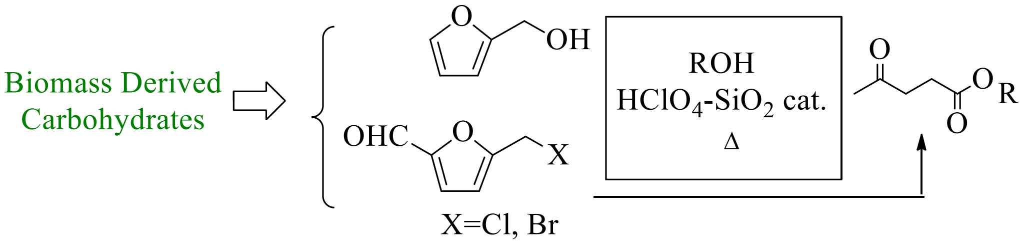


1-6

Methyl levulinate **1** (n=0); Ethyl levulinate **2** (n=1); Propyl levulinate **3** (n=2)
Butyl levulinate **4** (n=3); Pentyl levulinate **5** (n=4); Hexyl levulinate **6** (n=5)

Scheme 6.1 Esterification of LA using the HPA catalysts.

Furthermore, the effect of the molar ratio of reagents, reaction temperature, duration, and catalyst loading on the selectivity and isolated yield of ALs have been studied. In the second strategy, a series of ALs were prepared from biomass-derived furfuryl alcohol and XMF (X=Cl, Br) using a heterogeneous acid catalyst. XMF (X=Cl, Br) are hydrophobic congeners of HMF. As mentioned earlier, the separation and purification of CMF and BMF from the aqueous reaction media are relatively straightforward (Hibbert et al. 1923, Le et al. 2017, Mascal 2019). The ALs can be prepared conveniently by the alcoholysis of CMF or BMF, whereas the HCl and HBr byproduct may be recycled to produce more CMF and BMF, respectively. Besides, the alcoholysis of CMF or BMF is an irreversible reaction and do not produce water as a byproduct, unlike the acid-catalyzed esterification of LA. Mascal et al. produced EL in 85% isolated yield by reacting CMF with excess ethanol (anhydrous, 200 proof). The reaction was conducted at 160 °C in a glass pressure reactor (Mascal et al. 2010). To the best of our knowledge, the syntheses of ALs of higher alkyl chain length from CMF or BMF are not reported in the literature. Methyl levulinate (ML) could easily be obtained by refluxing CMF or BMF in anhydrous methanol. However, the conversion of CMF or BMF did not reach 100% even after prolonged heating in excess anhydrous 1-butanol, and butyl levulinate (BL) had to be separated from the unreacted CMF by column chromatography. The lower reactivity of alcohols with CMF or BMF became more prominent with increasing alkyl chain length. We envisioned that an acid catalyst would likely promote the furan ring-opening in CMF and BMF. In this regard, perchloric acid ($HClO_4$) is a strong Brønsted acid (pKa = -8), which has a non-nucleophilic counter anion. The acid has high thermal stability and is recoverable by vacuum distillation. In recent years, perchloric acid supported on silica gel ($HClO_4$-SiO_2) has been used as an efficient heterogeneous catalyst for various chemical transformations (Dalpozzo et al. 2010). Interestingly, $HClO_4$-SiO_2 has recently been used as a catalyst for the esterification of LA into ALs (Yang et al. 2019). In this study, we report the synthesis of a series of ALs directly from biomass-derived CMF, BMF, and furfuryl alcohol in excellent isolated yields using $HClO_4$-SiO_2 catalyst **(Scheme 6.2)**. The reaction was optimized on the temperature, duration, molar ratio of reagents, and catalyst loading.



Scheme 6.2 Preparation of ALs from biomass-derived furanics using the $HClO_4$-SiO_2 catalyst.

6.2 EXPERIMENTAL SECTION

6.2.1 Materials

Levulinic acid (98%) was purchased from Avra Synthesis Pvt. Ltd. Methanol (99.5%), ethanol (99%), 1-propanol (99.5%), 1-butanol (99%), and chloroform (99%), Silica gel (200-400 mesh) were purchased from Loba Chemie. Pentanol, Furfuryl alcohol, hexanol, and Perchloric acid (72% aq.) were purchased from Spectrochem. Phosphotungstic acid ($H_3PW_{12}O_{40}$), Silicotungstic acid ($H_4SiW_{12}O_{40}$), and Phosphomolybdic acid ($H_3PMo_{12}O_{40}$) were purchased from Sigma. Furfuryl alcohol (99%) was distilled under vacuum before use. The alcohols were used after overnight drying over pre-activated molecular sieves (4 Å). The catalysts were dried at 110 ºC for 12 h in a hot-air oven prior use.

6.2.2 Preparation of the $HClO_4$-SiO_2 Catalyst

The catalyst was prepared by following a literature procedure (Ansari et al. 2012). Perchloric acid (4.00 g, 72% aq.) was added drop-wise to a suspension of silica gel (200-400 mesh, 20.01 g) in diethyl ether (150 mL) under vigorous magnetic stirring. The mixture was stirred overnight at room temperature. Diethyl ether was removed in a rotary evaporator, and the silica gel was heated at 110 °C for 72 h to produce $HClO_4$-SiO_2 as a white, free-flowing powder.

6.2.3 METHOD A: Preparation of ALs from LA using the HPA catalyst

LA (1.010 g, 8.70 mmol) and a 1-butanol (0.968 g, 13.05 mmol, 1.5 eq.) were charged into a round-bottomed glass pressure reactor fitted with a magnetic stir rod and Teflon screw top. Oven-dried PTA (100 mg, 10 wt%) was weighed in air and added to the solution. The reactor was sealed and placed in a pre-heated (120 °C) oil bath and stirred magnetically for 6 h. After the reaction, the reactor was cooled to room temperature and opened. The mixture was carefully transferred into a centrifugation tube, and chloroform (10 mL) was added. The suspension was centrifuged at 800 rpm for 10 min. The supernatant liquid was transferred into a round bottom flask. The precipitate was washed with fresh chloroform. The chloroform fractions were combined, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure in a rotary evaporator. The crude mixture was chromatographed (silica gel, chloroform), and the solvent evaporated to get BL (1.362 g, 91%) as a clear liquid.

6.2.4 METHOD B: Synthesis of ALs from biomass-derived furanics using $HClO_4$-SiO_2

6.2.4.1 Synthesis of AL (C1-C4) from CMF

CMF (0.500 g, 3.46 mmol), ethanol (10 mL), and $HClO_4$-SiO_2 (0.020 g, 0.028 mmol, 0.828 mol%) were charged into a 75 mL cylindrical glass pressure vessel. The reactor was then sealed, placed in a pre-heated (120 °C) oil-bath, and magnetically-stirred continuously for 6 h. After the reaction, the reactor was cooled down to room temperature. The reaction mixture was diluted with chloroform (10 mL), and the solid $HClO_4$-SiO_2 catalyst was filtered off. The crude mixture was decolorized by adding activated charcoal. The solution was filtered, and the filtrate was evaporated under vacuum to afford EL as a brown liquid. The crude product was chromatographed (Silica gel, chloroform). Evaporation of chloroform under reduced pressure provided EL as light yellow oil (0.450 g, 90%). The same procedure, when applied to BMF, afforded EL in 91% isolated yield.

6.2.4.2 Synthesis of AL (C5-C6) from CMF

In a typical process, CMF (0.502 g, 3.46 mmol), 1-pentanol (1.22 g, 13.84 mmol), and $HClO_4$-SiO_2 (0.020 g, 0.828 mol%) were charged into a 10 mL round-bottomed flask fitted with a water-cooled condenser. The reaction mixture was placed in a pre-heated (120 °C) oil bath and magnetically stirred continuously for 6 h. After completion of the reaction, the mixture was cooled down to room temperature. The solid $HClO_4$-SiO_2 was filtered off, and the crude mixture was decolorized by adding activated charcoal. The solution was filtered, and the filtrate was evaporated under vacuum to afford PL as a brown liquid. The crude product was chromatographed (Silica gel, petroleum ether). Evaporation of solvent provided PL as a yellow oil (0.580 g, 90%). The same procedure provided PL in 92% yield when BMF was used as the starting material.

6.2.4.3 Synthesis of AL (C1-C4) from furfuryl alcohol

Furfuryl alcohol (0.500 g, 5.09 mmol), ethanol (10 mL) and $HClO_4$-SiO_2 (0.020 g, 0.028 mmol, 0.550 mol%) were charged into a 75 mL cylindrical glass pressure vessel. The reactor was then placed in a pre-heated (120 °C) oil-bath and magnetically stirred continuously for 6 h. After completion of the reaction, the reactor was cooled down to room temperature. The solid $HClO_4$-SiO_2 was filtered off and washed with petroleum ether. The solution was filtered, and the filtrate (solution) was evaporated under vacuum to afford the product EL as a brown liquid. The crude product was chromatographed (Silica gel, petroleum ether). Evaporation of solvent provided EL as a light yellow liquid (0.617 g, 84%).

6.3 IDENTIFICATION AND CHARACTERIZATION OF THE SYNTHESIZED CATALYST AND ALs

The alkyl levulinates were characterized by FTIR and NMR (^{1}H & ^{13}C) spectroscopy. Fourier Transform Infrared (FTIR) spectra were recorded on a Bruker Alpha 400 FTIR spectrometer, which is equipped with silicon-carbide as an IR source. All sample spectra were recorded using the ATR technique. The samples under study were recorded with 24 scans having a sample resolution of 4 cm^{-1}. The ^{1}H-NMR spectra of methyl- to butyl levulinate were recorded on a Bruker 400 MHz spectrometer using deuterated chloroform as the solvent. The ^{13}C-NMR spectra were recorded in the same instrument at a calculated frequency of 100 MHz. The ^{1}H - NMR spectra of pentyl- and hexyl levulinate were recorded on a Bruker Nano Bay 300 MHz spectrometer using deuterated chloroform as the solvent. The ^{13}C-NMR spectra were recorded in the same instrument at a calculated frequency of 75 MHz. Chemical shifts are provided in parts per million and coupling constants in Hertz. The scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) is a powerful tool to know the morphology and their relative proportion in materials under study. The SEM-EDX characterization of the catalyst was performed in a JEOL JSM-6380LA instrument operating at 20 kV. The powder X-ray diffraction (PXRD) analysis is used to know the crystallinity or amorphous behavior of a material. This also shows the phase change behavior of a catalyst during the reaction. The PXRD analysis was performed in a Rigaku MiFlex600 X-ray diffraction. The thermogravimetric analysis (TGA) is used to know the thermal stability of an organic compound or an inorganic catalyst. The TGA data of the catalyst obtained with the PerkinElmer TGA 4000 instrument.

6.3.1 Characterization of synthesized $HClO_4$-SiO_2 catalyst

The catalyst was characterized by FTIR spectroscopy **(Figure 6.1)**. The results display the peaks at ∼1092, and 800 cm^{-1} are attributed to asymmetric and symmetric stretching vibrations of Si-O, respectively. The broad peak nearly 3450cm $^{-1}$ corresponding to the stretching vibration of surface O-H, which might directly connect with the introduced $HClO_4$ groups by electrostatic and chemical interaction. As compared to the pure SiO_2, the FTIR spectrum of $HClO_4$-SiO_2 catalyst in KBr disk showed a characteristic peak of Cl-O bond stretching at 629 cm^{-1}, indicating the efficient incorporation of $HClO_4$ on SiO_2 (Ansari et al. 2012, Chakraborti et al. 2003, Yang et al. 2019).

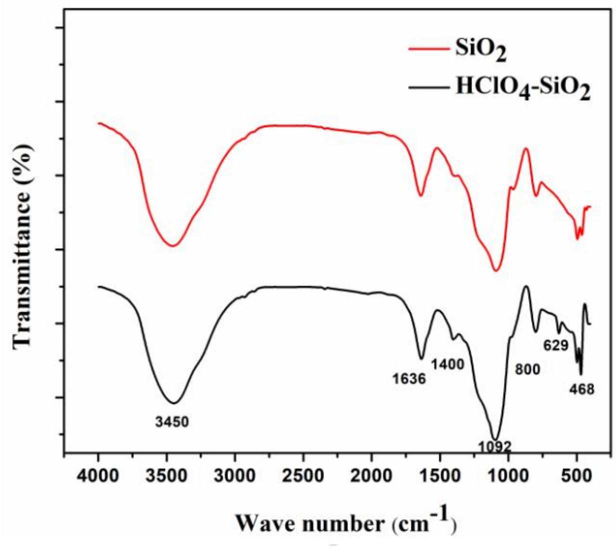


Figure 6.1 The FTIR spectra of SiO_2 (200-400 mesh) and 20 wt% $HClO_4$-SiO_2.

The characterization data matched with the literature report and conclusively proved the presence of perchlorate ion in the silica gel matrix. The PXRD spectrum of both SiO_2 and $HClO_4$-SiO_2 catalyst showed a broad diffraction peak around 20 to 30° that implies that the amorphous nature of silica gel was preserved **(Figure 6.2)**.

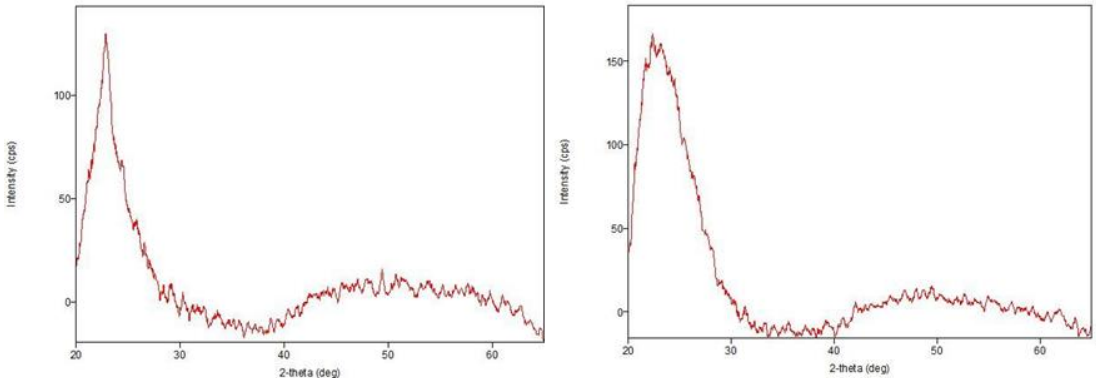
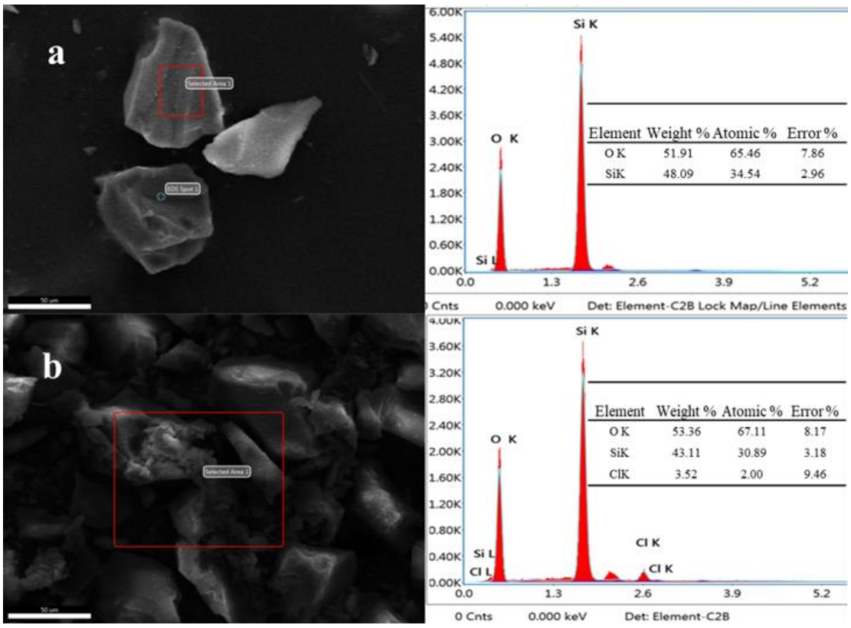


Figure 6.2 Powder X-Ray Diffraction (PXRD) of pure SiO_2 (left) and the $HClO_4$-SiO_2 catalyst (right).

Further, the SEM analysis images of the silica gel matrix and $HClO_4$-SiO_2 catalyst showed the surface immobilization of perchloric acid on silica gel. And the EDX study conclusively showed the presence of perchlorate anion in the silica gel matrix, as displayed in **Figure 6.3**.



Element	Weight %	Atomic %	Error %
O K	51.91	65.46	7.86
SiK	48.09	34.54	2.96

Element	Weight %	Atomic %	Error %
O K	53.36	67.11	8.17
SiK	43.11	30.89	3.18
ClK	3.52	2.00	9.46

Figure 6.3 The SEM image (left) and EDX data (right) of a) pure SiO_2 (200-400 mesh) and b) $HClO_4$-SiO_2 catalyst.

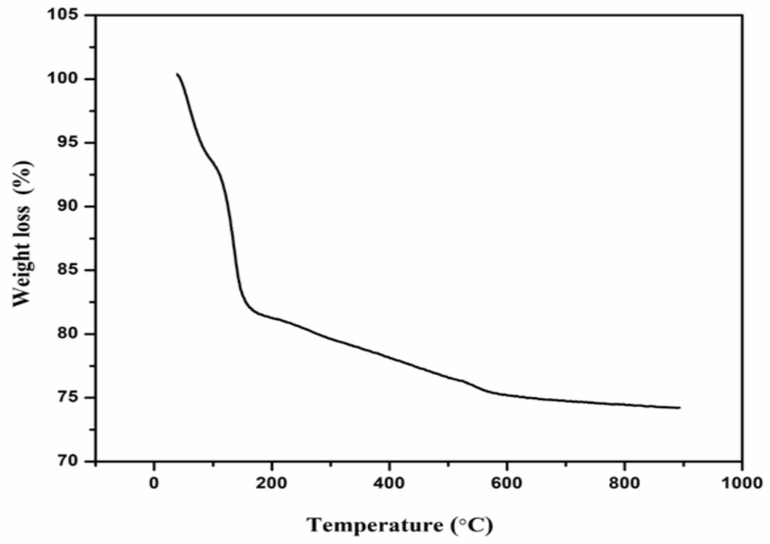


Figure 6.4 The TGA curve of $HClO_4$-SiO_2.

TGA analysis of the prepared $HClO_4$-SiO_2 catalyst matched well with the literature data (Yang et al. 2019**) (Figure 6.4)**. A 20.0% weight loss near 200 °C is due to the water loss, which is trapped in the supported framework. Further, an increase in temperature up to 500 °C did not show any other significant weight loss confirms the stability of the catalyst.

6.3.2 FTIR, ^1H-NMR and ^{13}C-NMR spectra of methyl levulinate (ML)

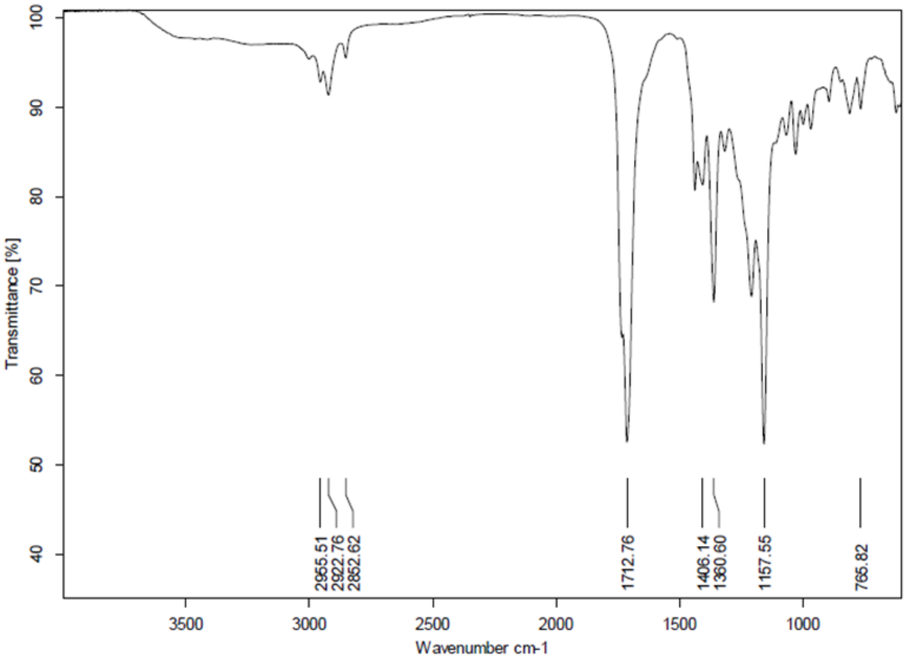


Figure 6.5 The FTIR spectrum of ML.

The peaks around 2852-2955 cm^{-1} show the stretching vibrations of the methylene (-CH_2) and methyl (-CH_3) groups (symmetric and antisymmetric). The strong peak at 1712 cm^{-1} is due to the –C=O stretching frequency of the ester group. The peak around 1157 cm^{-1} shows the stretching vibration of the carbonyl group (from both ketone and ester functionality).

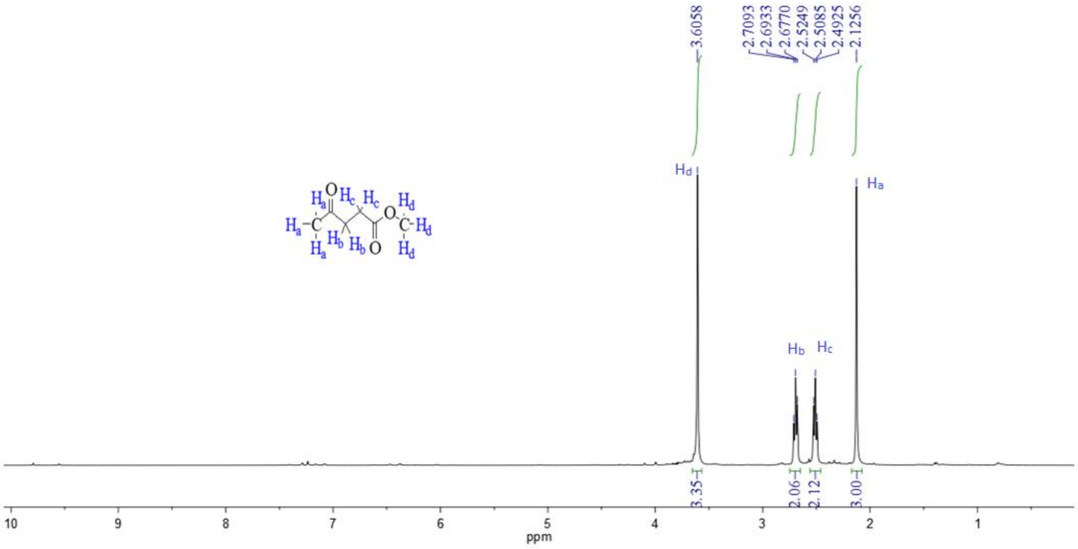


Figure 6.6 The ^{1}H-NMR spectrum of ML.

The ^{1}H-NMR spectrum of the isolated ML shows a singlet at 3.60 ppm for 3H corresponding to the deshielded protons of the -OCH_3 group, the two triplets at 2.69 ppm and 2.51 ppm for 2H each (J= 6.4) correspond to two -CH_2 groups present in between the ester and ketone functional group. The singlet at 2.12 ppm (3H) is due to the -CH_3 group directly attached to the keto group.

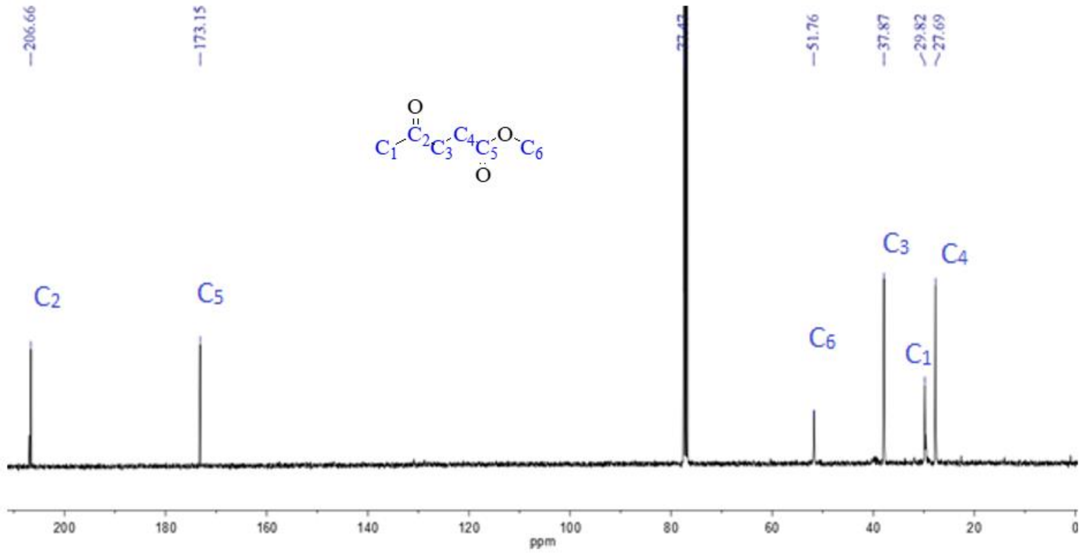


Figure 6.7 The ^{13}C-NMR spectrum of ML.

^{13}C-NMR of the isolated ML show the peak at 206.7 ppm corresponding to the ketone carbon (C=O), the peak at 173.1 ppm corresponding to the carbonyl carbon of the ester group. The peak at 51.7 ppm is attributed to the carbon of -OCH_3 group, and the peaks at 37.8 ppm and 29.8 ppm are due to the two deshielded methyl carbon attached to the keto group. The peak at 27.7 ppm corresponding to -CH_2- group attached to the ester carbonyl carbon.

6.3.3 FTIR, ^{1}H-NMR and ^{13}C-NMR spectra of ethyl levulinate (EL)

^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.09 (q, 2H, *J* = 7.2 Hz), 2.71 (t, 2H, *J* = 6.4 Hz), 2.52 (t, 2H, *J* = 6.4 Hz), 2.15 (s, 3H), 1.21 (t, 3H, *J* = 7.2 Hz);^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 202.4, 172.0, 59.6, 36.9, 28.8, 27.0, 13.1; FTIR (ATR, cm^{-1}): 2982, 2931, 1716, 1155.

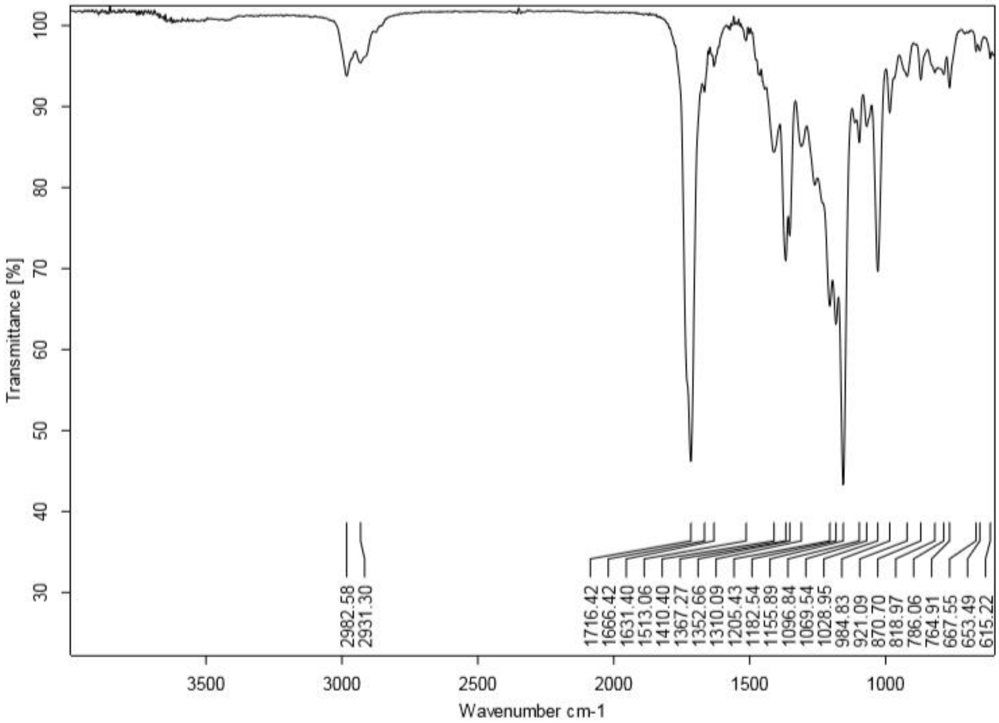


Figure 6.8 The FTIR spectrum of EL.

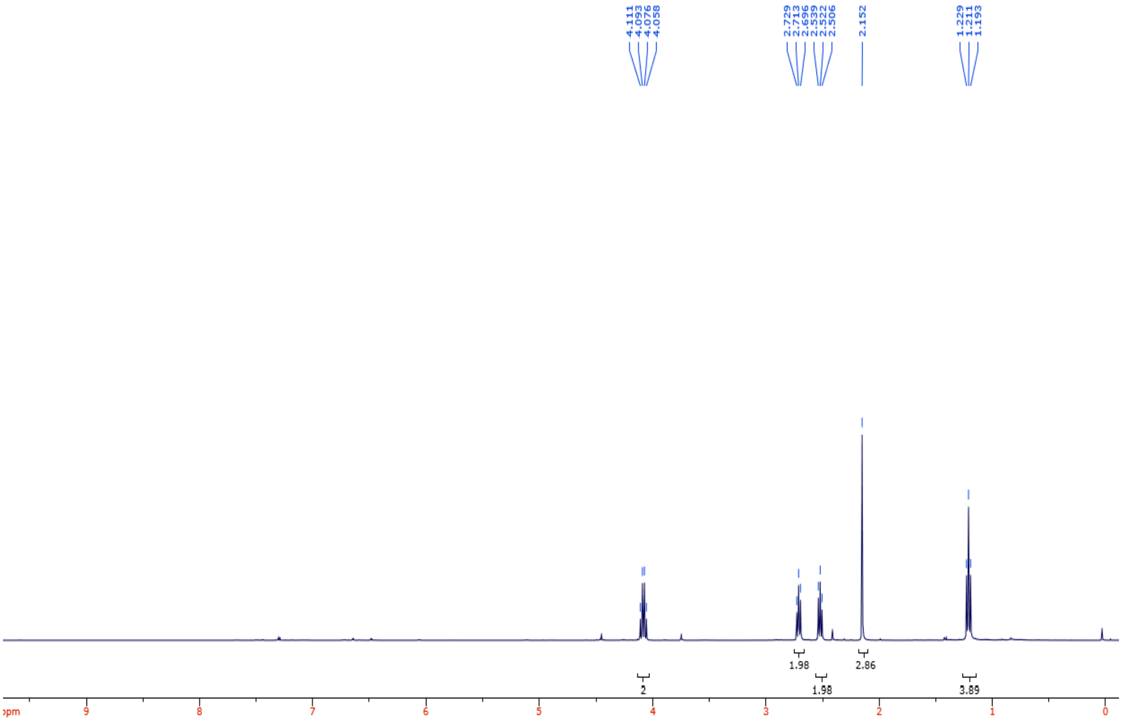


Figure 6.9 The ^{1}H-NMR spectrum of EL.

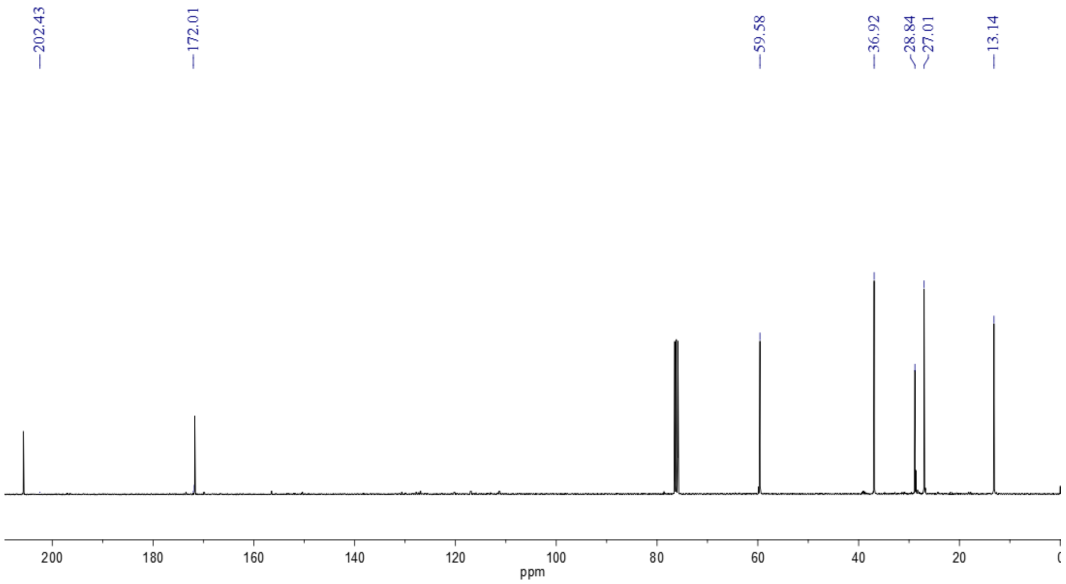


Figure 6.10 The ^{13}C-NMR spectrum of EL.

6.3.4 FTIR, ^{1}H-NMR and ^{13}C-NMR spectra of propyl levulinate (PrL)

^{1}H-NMR (CDCl$_3$, 400 MHz) δ (ppm): 3.95 (t, 2H, J = 5.0 Hz), 2.69 (t, 2H, J = 4.8 Hz), 2.49 (t, 2H, J = 4.8 Hz), 2.12 (s, 3H), 1.56 (m, 2H), 0.86 (t, 3H, J = 5.6 Hz);^{13}C-NMR (CDCl$_3$, 100 MHz) δ (ppm): 206.6, 172.7, 66.1, 37.8, 29.7, 27.9, 21.8, 10.2; FTIR (ATR, cm^{-1}): 2969, 2940, 1715, 1358, 1155.

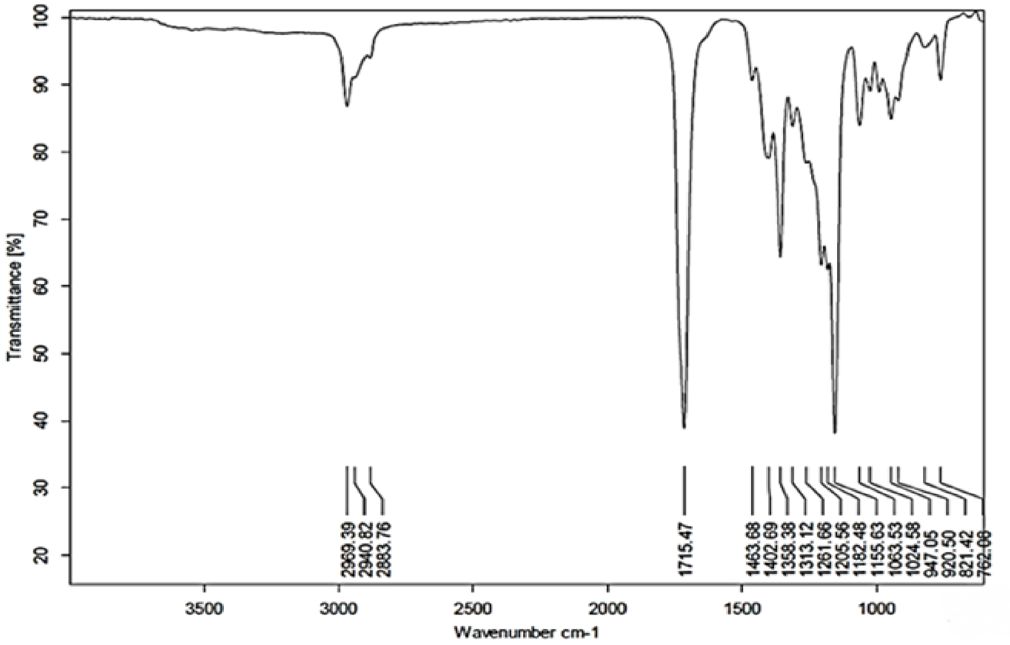


Figure 6.11 The FTIR spectrum of PrL.

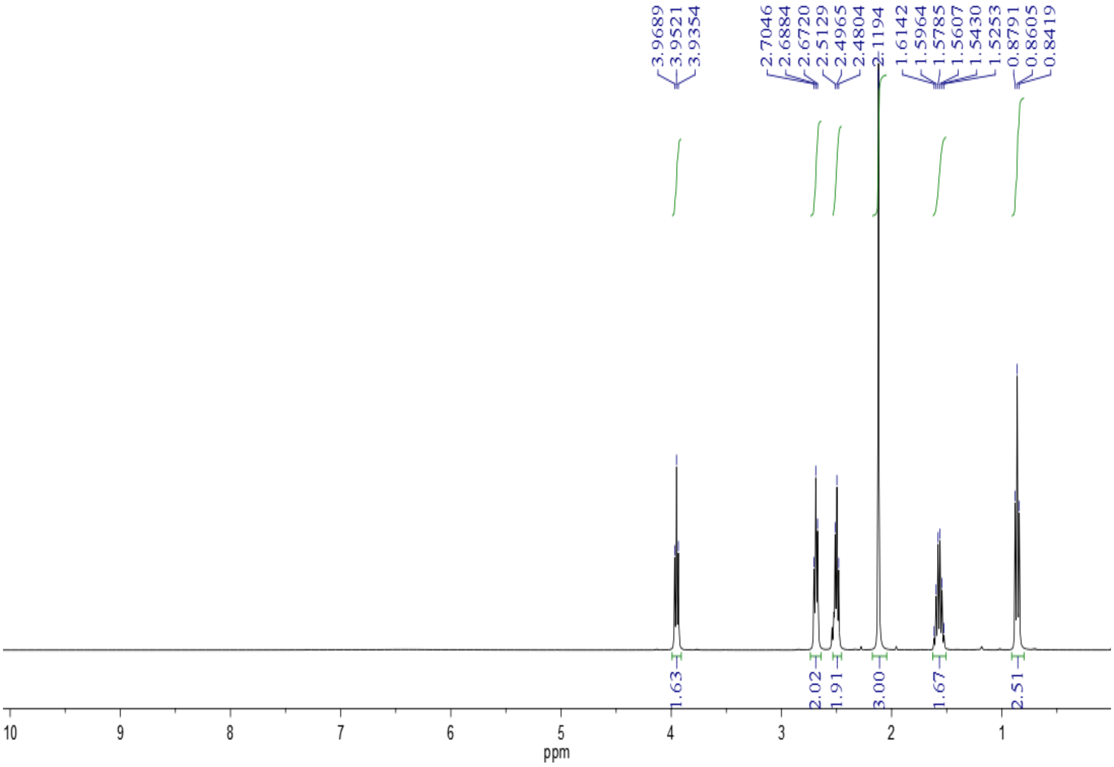


Figure 6.12 The ^{1}H-NMR spectrum of PrL.

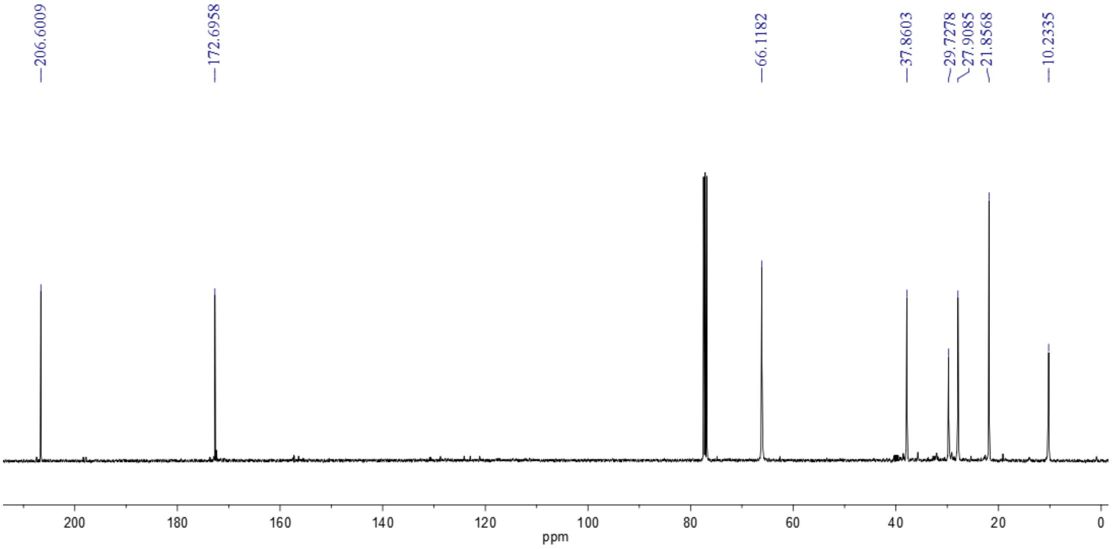


Figure 6.13 The ^{13}C-NMR spectrum of PrL.

6.3.5 FTIR, ^{1}H-NMR and ^{13}C-NMR spectra of butyl levulinate (BL)

^{1}H-NMR (CDCl$_3$, 400 MHz) δ (ppm): 4.04 (t, 2H, *J* = 6.8 Hz), 2.72 (t, 2H, *J* = 6.4 Hz), 2.54 (t, 2H, *J* = 6.4 Hz), 2.16 (s, 3H), 1.56 (m, 2H), 1.34 (m, 2H), 0.90 (t, 3H, *J* = 8.0 Hz);^{13}C-NMR (CDCl$_3$, 100 MHz) δ (ppm): 206.6, 172.7, 64.5, 37.9, 30.5, 29.8, 27.9, 19.0, 13.6; FTIR (ATR, cm^{-1}): 2960, 2935, 1716, 1357, 1158.

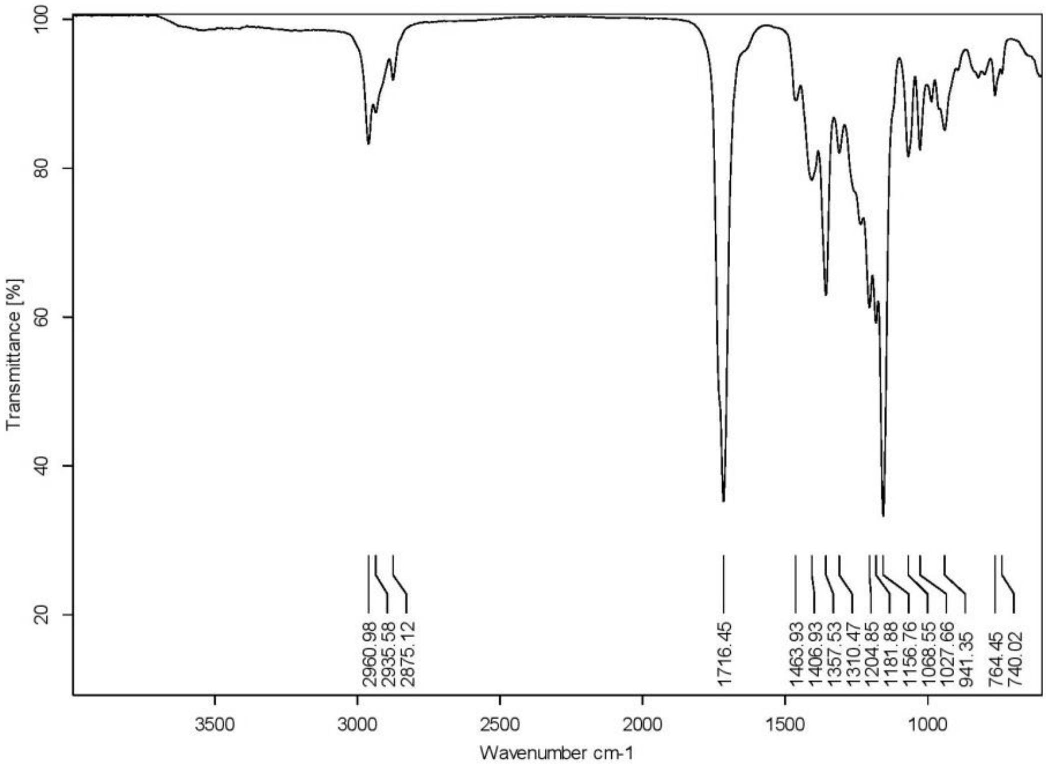


Figure 6.14 The FTIR spectrum of BL.

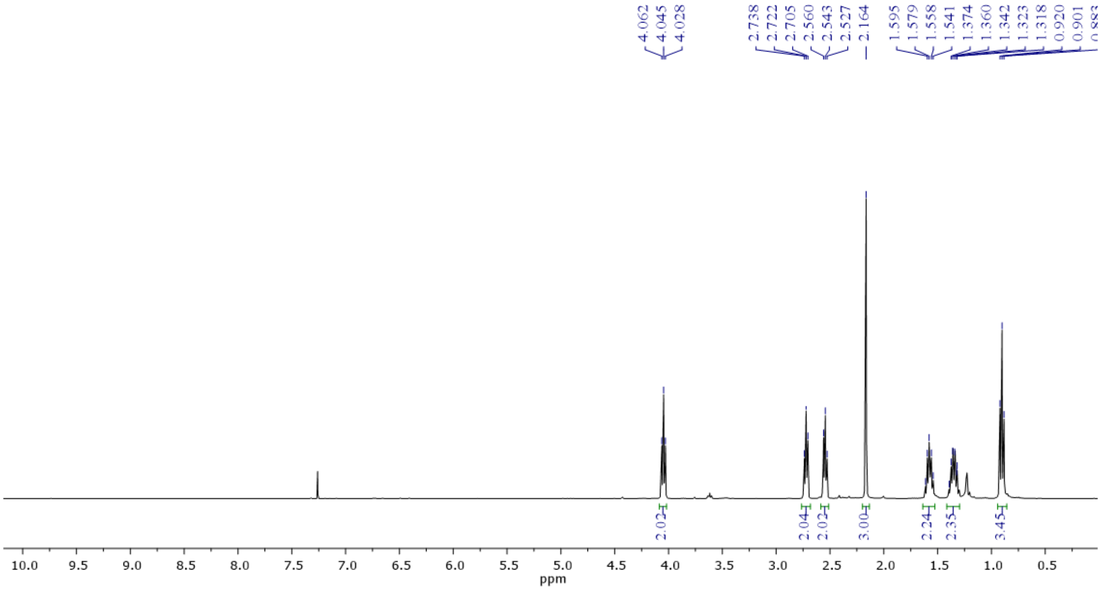


Figure 6.15 The ^{1}H-NMR spectrum of BL.

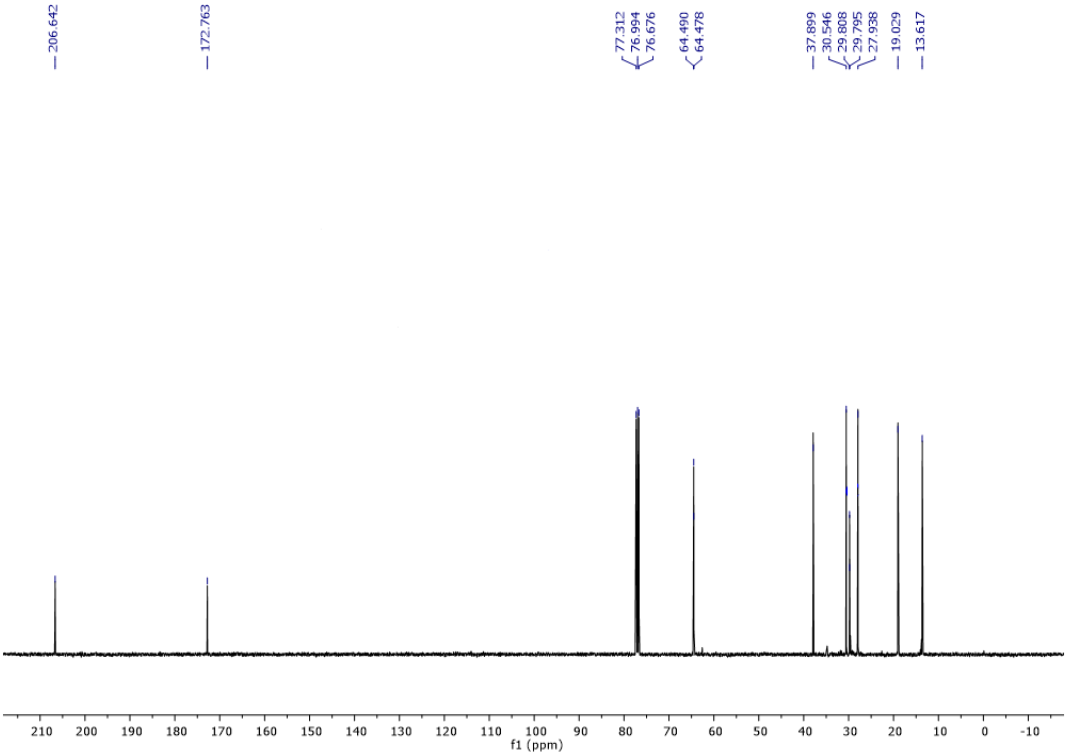


Figure 6.16 The ^{13}C-NMR spectrum of BL.

6.3.6 FTIR, ^{1}H-NMR and ^{13}C-NMR spectra of pentyl levulinate (PL)

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 4.01 (t, 2H, *J* = 6.7 Hz), 2.69 (t, 2H, *J* = 6.6 Hz), 2.49 (t, 2H, *J* = 6.6 Hz), 2.12 (s, 3H), 1.56 (m, 2H), 0.84 (t, 3H, *J* = 6.8 Hz);^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 206.8, 172.8, 64.8, 37.9, 29.7, 28.2, 27.9, 27.6, 22.2, 13.9; FTIR (ATR, cm^{-1}): 2958, 2933, 1716, 1357, 1156.

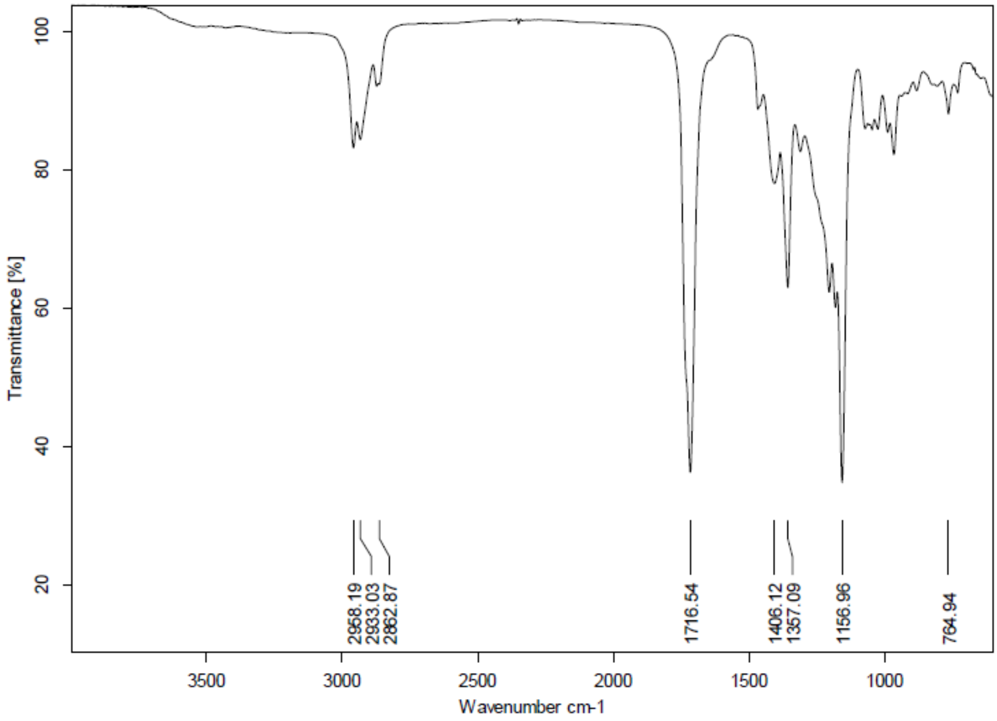


Figure 6.17 The FTIR spectrum of PL.

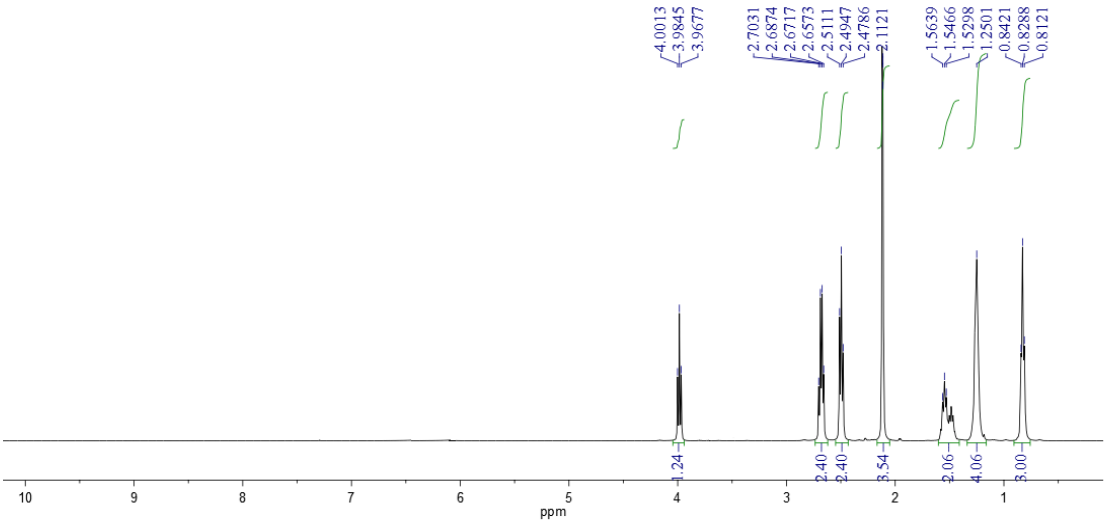


Figure 6.18 The ^{1}H-NMR spectrum of PL.

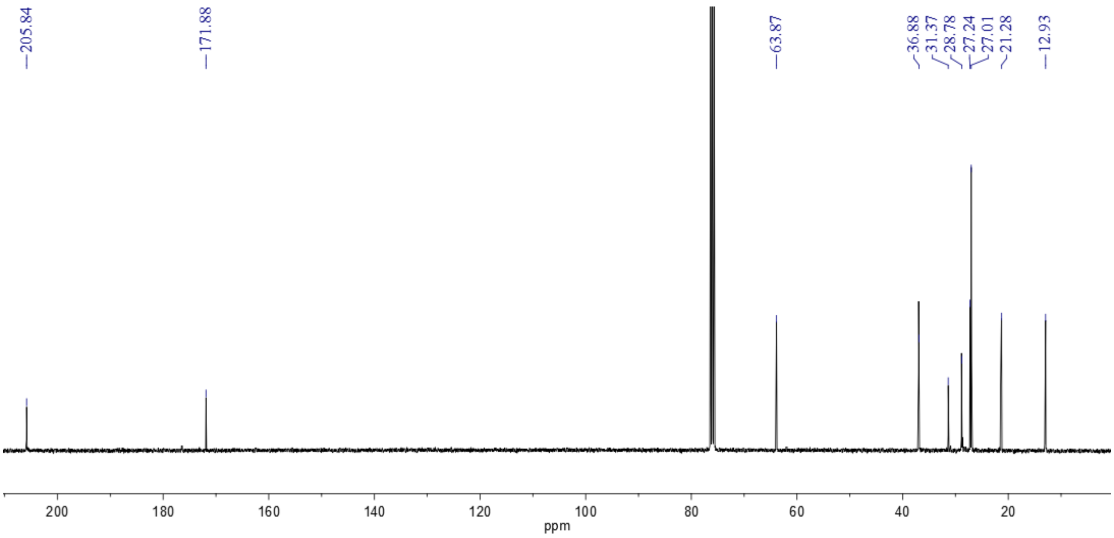


Figure 6.19 The ^{13}C-NMR spectrum of PL.

6.3.7 FTIR, ^{1}H-NMR and ^{13}C-NMR spectra of hexyl levulinate (HL)

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 3.99 (t, 2H, *J* = 6.6 Hz), 2.68 (t, 2H, *J* = 6.9 Hz), 2.49 (t, 2H, *J* = 6.9 Hz), 2.12 (s, 3H), 1.54 (m, 2H), 1.23 (m, 6H), 0.82 (t, 3H, *J* = 6.6 Hz);^{13}C-NMR ($CDCl_3$,75 MHz) δ (ppm): 206.7, 172.8, 64.8, 37.9, 31.4, 29.8, 28.5, 27.9, 25.5, 22.5, 13.9; FTIR (ATR, cm^{-1}): 2956, 2930, 1719, 1356, 1156.

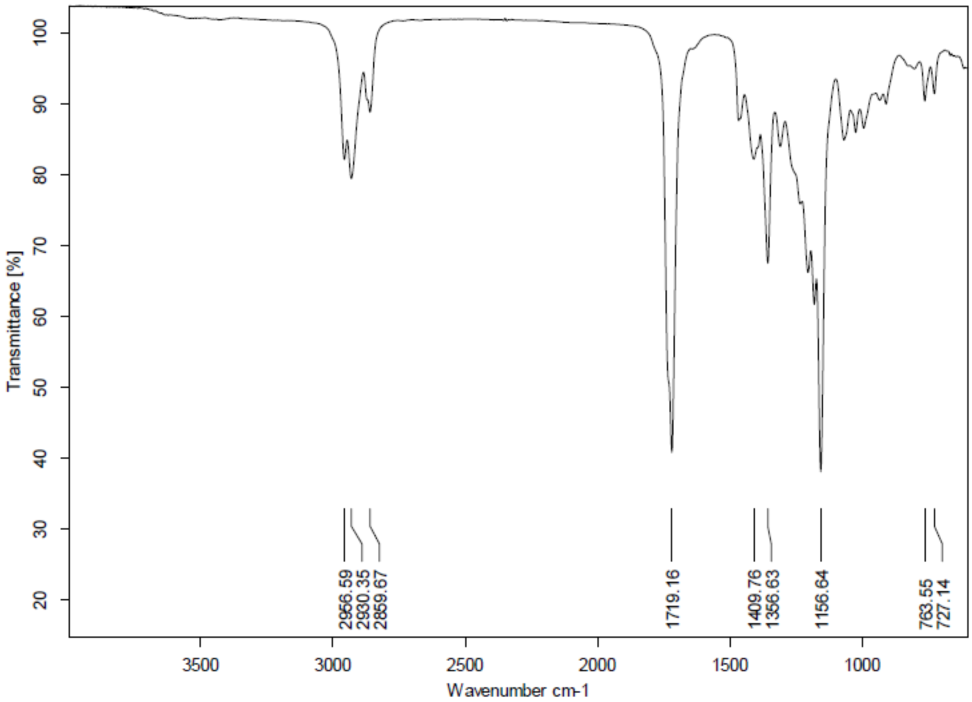


Figure 6.20 The FTIR spectrum of HL.

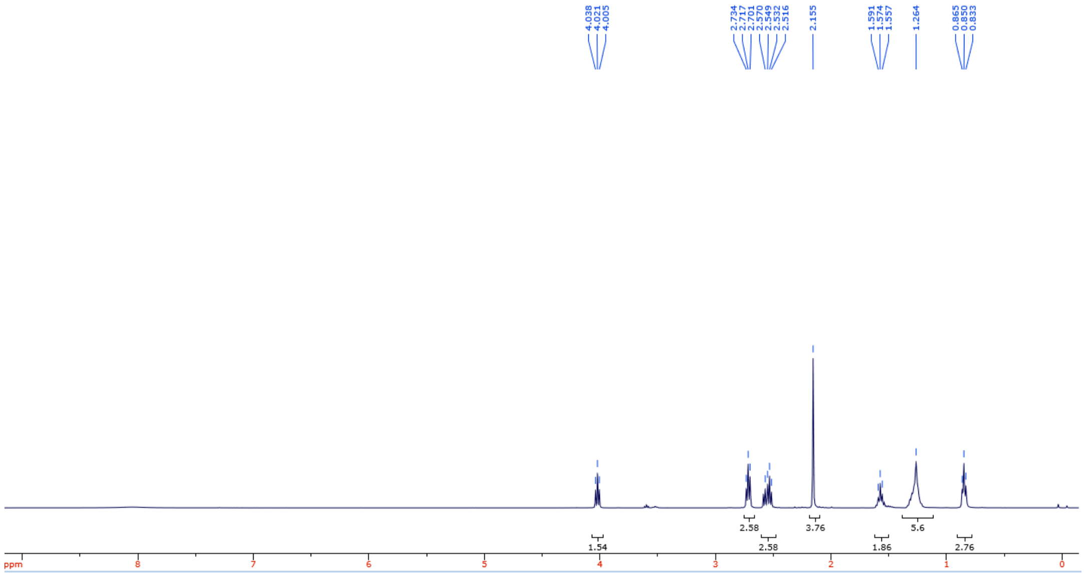


Figure 6.21 The ^{1}H-NMR spectrum of HL.

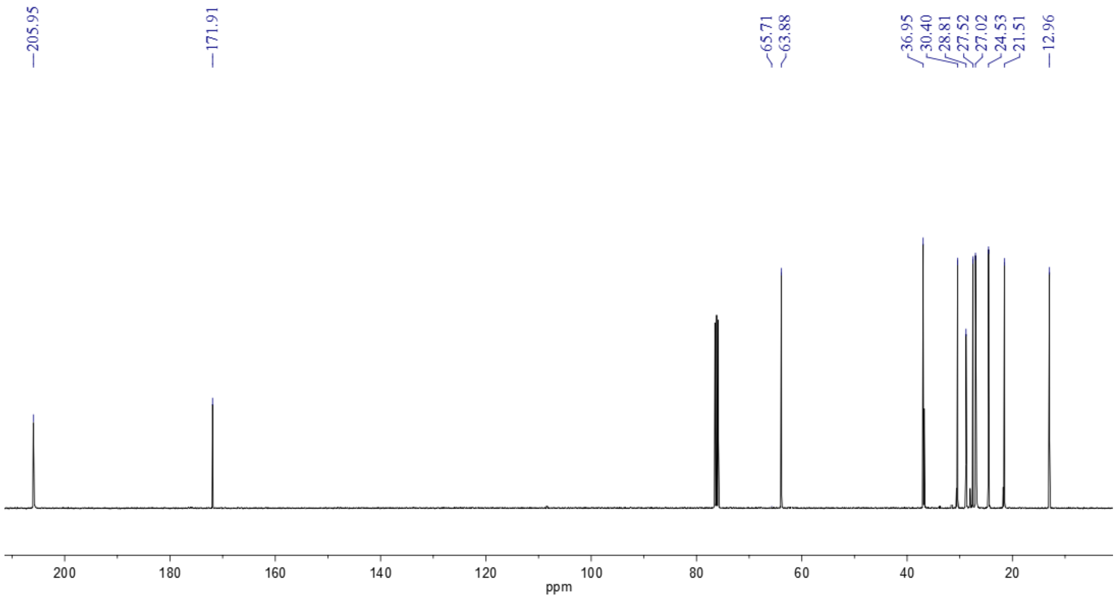


Figure 6.22 The ^{13}C-NMR spectrum of HL.

6.4 RESULTS AND DISCUSSION

6.4.1 Synthesis of ALs from LA using HPA

In order to find the best reaction conditions, the conversion of LA into ALs was investigated using different HPA catalysts, LA to alcohol ratios, reaction temperature, and duration of the reaction. Butyl levulinate (BL) was chosen as the model substrate for reaction optimization. A detailed experimental observation on parametric optimization is discussed below.

6.4.2 Effect of reaction temperature on the preparation of BL

The effect of temperature on the synthesis of BL was investigated using PTA catalyst. The reaction produced BL only in trace amount even after stirring for 12 h at room temperature. Increasing the temperature to 80 °C afforded only a 50% yield of BL **(Figure 6.23)** after 6 h. Upon increasing the temperature to 90 °C and 100 °C, the yield of BL increased to 72% and 84%, respectively. The mass balance was essentially the unreacted LA. The yield of BL reached the maximum (ca. 90%) at 120 °C. The ^{1}H-NMR spectrum of the crude product did not show any unreacted LA.

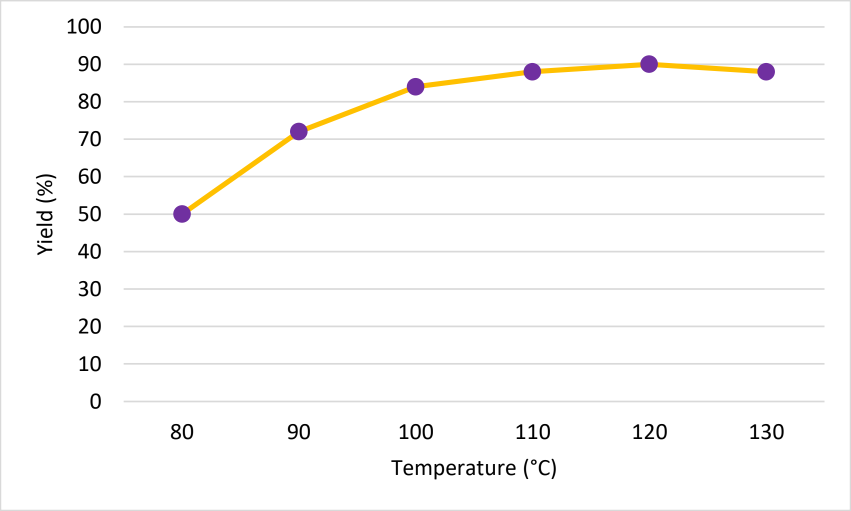


Figure 6.23 Effect of reaction temperature on the isolated yield of BL.

Reaction conditions: LA: alcohol=1:1.5 (molar ratio), 6 h, 10 wt% PTA.

6.4.3 Effect of the molar ratio of LA and butanol on BL yield

In order to investigate the effect of the molar ratio of LA and 1-butanol on the yield of BL, the reaction was carried out at 120 °C for 6 h using 10 wt% of phosphotungstic acid (PTA) as the catalyst. The molar ratio of LA to 1-butanol was varied from 1:3 to 1:1. The results show **(Figure 6.24)** that the yields of BL at ratios above 1:1.5 is nearly constant. However, using a lesser quantity of 1-butanol significantly lowers the yield of BL due to the incomplete reaction.

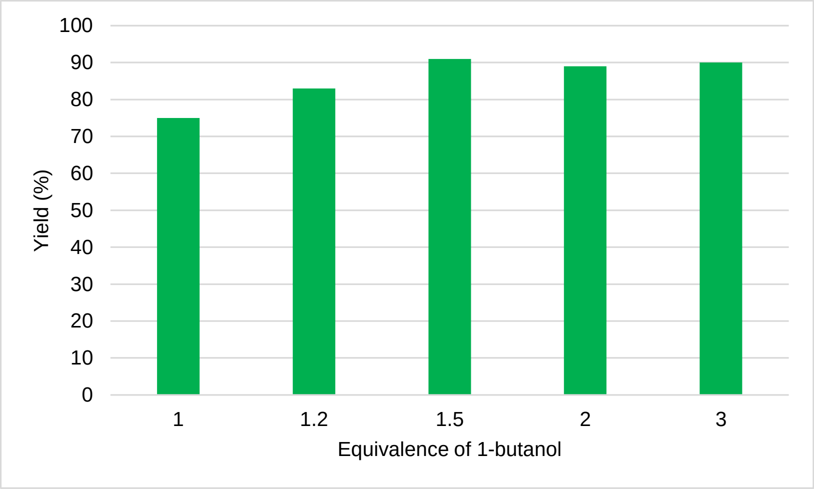


Figure 6.24 The effect of equivalence of 1-butanol on the isolated yield of BL. **Reaction conditions**: LA (10mmol), 120 °C, 6 h, 10 wt% PTA.

6.4.4 Synthesis of alkyl levulinates using different HPAs

The esterification reaction was independently carried out using three commercially-available HPAs, namely, phosphotungstic acid (PTA), silicotungstic acid (STA) and phosphomolybdic acid (PMA). The esterification of LA with ethyl alcohol, 1-butanol, and 1-hexanol was carried out at 120 °C for 6 h using 10 wt% (compared to LA used) of HPAs. Among the three HPAs examined, PTA was found to be the most effective catalyst for all three alcohols. Use of PTA as catalyst afforded ethyl levulinate (EL) in 92% yield, whereas PMA and STA afforded the same in 75% and 69% respectively, under identical conditions **(Figure 6.25)**. The trend was found to be similar for BL and hexyl levulinate (HL) as well. PTA as catalyst provided 90% and 92% of BL and HL, respectively, whereas STA provided them in 74% and 75% yields. PMA was found to have intermediate efficiency in producing alkyl levulinates. The difference in reactivity of these three catalysts tried can be explained by their order of acidity where PTA being the most and STA being the least acidic.

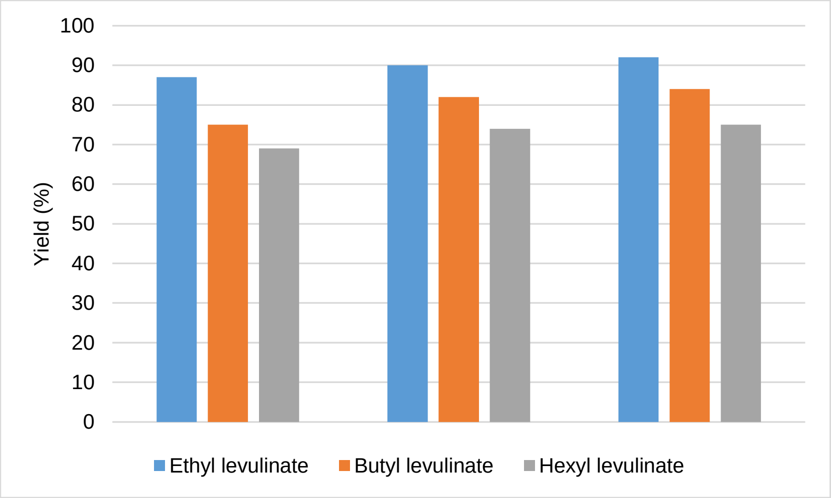


Figure 6.25 The efficiency of various HPAs on the yield of ALs.

Reaction conditions: LA (10 mmol), alcohol (15 mmol), 120 °C, 6 h, 10 wt% catalyst. EL (left), BL (middle), HL (right).

Further, a study on catalyst optimization revels that the BL yield increases linearly with an increase in catalyst loading. For catalyst loading above 10 wt%, the yield increases only marginally. However, at lower catalyst loading, the yield of BL decreases considerably. Thus, a maximum BL yield was achieved with 10 wt% of catalyst loading at 120 °C for 6 h. Hence the optimized reactions for BL were then applied for the production of methyl-hexyl levulinate from LA using PTA as a catalyst.

6.4.5 Synthesis of alkyl levulinates using different monohydric alcohols

The reactions were performed in a glass pressure tube fitted with Teflon screw top. The set up allows reaching temperature higher than the boiling point of the alcohol without evaporative loss of alcohol during the reaction. Under the optimized reaction conditions, methyl levulinates (ML) was isolated in 85% yield, and pentyl levulinates (PL) was obtained in 94% isolated yield **(Figure 6.26)**. In general, the yield of alkyl levulinates improved when alcohol with longer alkyl chain length was used. This trend can be explained by a higher chance of concomitant ether formation from alcohol in the presence of acid that is more pronounced in smaller alcohols like methanol.

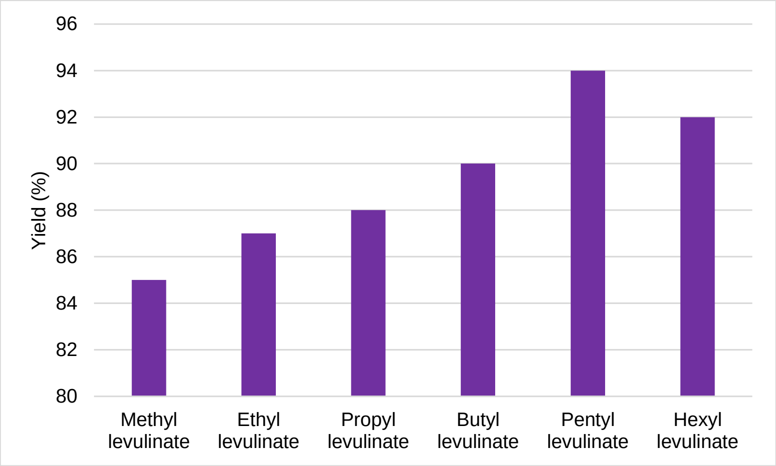


Figure 6.26 Preparation of ALs from LA.

Reaction conditions: LA: alcohol (1:1.5) (molar ratio), 120 °C, 6 h, 10 wt% PTA.

6.4.6 Study of catalyst recyclability

Recyclability of the catalyst is one of the important parameters for the scalability of the process, economic viability, and the green indices. The PTA catalyst was attempted to be recycled and reused for three consecutive runs. After the reaction, the catalyst was precipitated by diethyl ether and separated from the reaction mixture by centrifugation. The catalyst was then dried in an oven at 110 °C for 12 h before submitting for the consecutive runs. All consecutive runs with a recovered catalyst were carried out using the same catalyst/reactant ratio. The PTA catalyst was recycled successfully for three consecutive cycles without significant loss of activity. BL was isolated in 91%, 88%, and 85% yield over three consecutive cycles **(Table 6.1)**. In all three cycles, the physical recovery of the catalyst remained more than 90%. The structure of the recovered PTA catalyst remained intact, as confirmed by the ^{31}P-NMR spectroscopy.

Table 6.1 Recovery and reuse of PTA in the preparation of BL

Entry	Catalyst used (mg)[a]	Catalyst recovered (mg)	Yield (%)[b]
1	100	91	91
2	100	92	87

3	100	90	85

[a] The recovered catalyst from multiple trials were combined to ensure that the same amount of catalyst in used in each consecutive cycle, [b] isolated yield.

6.4.7 Synthesis of ALs from CMF or BMF

In order to find out the best-optimized reaction condition for the solvent-free, one-pot preparation of ALs from biomass-derived CMF, BMF, and furfuryl alcohol was investigated using various acid catalysts. The effect of reaction temperature, duration, the molar ratio of reagents, and loading of the catalyst was studied. BL was chosen as the product of choice for parametric optimization of the alcoholysis reaction. Detailed experimental outcomes were discussed in the following section.

6.4.8 Catalyst screening for the alcoholysis of CMF or BMF into ALs

Initially, attempts were made to synthesize EL by simply reacting CMF or BMF in excess ethanol. The reaction was monitored by TLC, and the products were characterized by both FTIR and ^{1}H-NMR spectroscopy. Interestingly, even after prolonged (6 h) heating at relatively high temperature (ca. 150 °C) in a sealed pressure reactor, the quantitative conversion of CMF or BMF was not achieved. Although the reaction mixture contained EL as the major product, both the starting material and EMF were present in noticeable amounts. Therefore, various acid-catalysts were used as an additive to explore their effectiveness in promoting the alcoholysis reaction **Table 6.2** shows the effect of various acid-catalysts used during the preparation of EL from CMF and BMF. When methanesulfonic acid (1 mol%) was used as a catalyst, the conversion of CMF into EL reached only 70% after 6 h at 120 °C. However, the isolation of the catalyst was challenging, and the yield of EL was rather low due to the formation of humin. The use of hydrochloric acid as catalyst did not complete the reaction even after 6 h at 120 °C. When PTA (1.1 mol%) was used as an acid catalyst, the quantitative conversion of CMF and BMF was achieved after 6 h at 120 °C, and EL was isolated in 69% and 73% yield from CMF and BMF, respectively. A noticeable amount of insoluble humin formed in the reaction. With lesser amounts of PTA, the reaction did not reach completion. When aqueous perchloric acid was used as catalyst, the reaction completed after 6 h at 120 °C. After the reaction, the excess alcohol was first removed under reduced pressure. Interestingly, humic material formed during the evaporation of alcohol. This observation may be explained by the increasing concentration of dissolved $HClO_4$ in ethanol. Therefore, in order to avoid building-up acid concentration during work-up, the crude reaction mixture was first diluted in water and the product extracted in chloroform. In this strategy, the EL was isolated in 83% and 84% yield from CMF and BMF, respectively. Since $HClO_4$ showed promising activity in the alcoholysis of CMF and BMF, the acid was made heterogeneous by supporting it on silica gel (200-400 mesh).

Table 6.2 The effect of various homogeneous acid catalysts in the preparation of EL from XMF

Entry	Substrate	Reaction conditions	Conversion/ Yield (%)
1	CMF	Ethanol (40 mL), 150 °C, 6 h	[40][a]
2	CMF	Ethanol (40 mL), $MeSO_3H$ (1.1mol%), 120 °C, 6 h	[70] [b]
3	CMF (BMF)	Ethanol (40 mL), PTA (1.1 mol%), 120 °C, 6 h	69 (73)[b]
4	CMF	Ethanol (40 mL), HCl (35%, 0.2 mL), 120 °C, 6 h	[50][a]
5	CMF (BMF)	Ethanol (40 mL), $HClO_4$(1.1 mol%), 120 °C, 6 h	83 (84)[b]
6	CMF (BMF)	Ethanol (40 mL), $HClO_4$-SiO_2(1.1mol%), 120 °C, 6 h	85 (88)[b]

[a] Conversion of CMF. [b] yield from CMF and BMF.

The supported catalyst worked better than perchloric acid itself with a better yield of EL under identical conditions along with the easier separation of product and isolation of the catalyst. In addition, the efficiency of the synthesized $HClO_4$-SiO_2 catalyst was compared with other solid acid catalysts, and their results are summarized in **Table 6.3**.

Table 6.3 The effect of various heterogeneous acid catalysts on the preparation of EL from XMF

Entry	Substrate	Reaction conditions	Conversion/ Yield (%)
1	CMF	0.5g silica-alumina (135), Ethanol (20 mL), 120 °C, 3 h, HPGR	[20][a]
2	CMF	20 wt% $AlCl_3$, Ethanol (20 mL), 80 °C, 12 h, (reflux)	[30] [a]
3	CMF	20 wt% Amberlyst 15(H), Ethanol (20 mL), 80 °C, 12 h, (reflux)	[50] [a]
4	CMF (BMF)	4 wt% $HClO_4$-SiO_2, Ethanol (10 mL), 120 °C, 6 h, HPGR	90 (91) [b]

[a] Conversion of CMF. [b] yield from CMF and BMF.

Among various Lewis and Brønsted solid acid catalysts examined for the ethanolysis of CMF or BMF, the strong Brønsted acid catalyst $HClO_4$-SiO_2 shows an excellent catalytic activity with 90 and 91% of EL yield from CMF and BMF respectively.

6.4.9 Effect of catalyst loading on BL yield

In order to find the best reaction conditions, the conversion of CMF or BMF into alkyl levulinates was optimized on catalyst loading. Initially, the effect of catalyst loading on the alcoholysis of CMF or BMF was studied by varying the catalyst dosage from 2-10 wt% (compared to XMF). The reaction was carried out for 6 h at 120 °C using excess (ca. 10 mL) of 1-butanol. The results are summarized in **Table 6.4**.

Table 6.4 Effect of $HClO_4$-SiO_2 loading on BL yield

Entry	Substrate	$HClO_4$-SiO_2 Catalyst loading (wt%)	BL Yield (%)
1	CMF (BMF)	2	-
2	CMF (BMF)	4	97 (97)

3	CMF (BMF)	6	96.5 (96.6)
4	CMF (BMF)	8	96.2 (96.5)
5	CMF (BMF)	3	94.1(95.3)
6	CMF (BMF)	10	94.3 (95.4)

As evident from the experimental results, 4 wt% of $HClO_4$-SiO_2 produce 97% of BL at 120 °C after 6 h with 10 mL 1-butanol. Thereafter, the increase in catalyst loading had no significant impact on the yield of BL. Thus, 4 wt% of $HClO_4$-SiO_2 was chosen as the optimum catalyst loading to get the maximum yield of AL starting from CMF or BMF.

6.4.10 Effect of reaction temperature and time on the yield of BL

The reaction temperature is one of the key factors that not only decides the energy requirement of the process but also modulates the rate of reaction, selectivity, and yield of the targeted product. Therefore, the synthesis of BL from CMF or BMF was studied at different reaction temperatures. It was noticed that the reaction did not proceed to completion at a lower temperature (<120 °C) even after 12 h **(Table 6.5).** A maximum of 97% of BL was archived from both CMF and BMF under optimized conditions (120 °C, 6 h, 4 wt% of $HClO_4$-SiO_2).

Table 6.5 The effect of reaction temperature on BL yield

Entry	Substrate	Temperature (°C)	BL Yield (%)
1	CMF (BMF)	80	-
2	CMF (BMF)	90	-
3	CMF (BMF)	100	88(93)
4	CMF (BMF)	110	91(95)
5	CMF (BMF)	120	97(97)

For a reaction temperature of 120 °C and 4 wt% of the $HClO_4$-SiO_2 catalyst, the optimal reaction time was found to be 6 h. Thereafter, no significant increase in BL yield was noticed. All the results are tabulated in **Table 6.6**.

Table 6.6 Effect of reaction time on the yield of BL

Entry	Substrate	Time (h)	Yield of BL (%)
1	CMF (BMF)	3	-
2	CMF (BMF)	6	97 (97)
3	CMF (BMF)	8	97 (96.4)
4	CMF (BMF)	10	96 (94)
5	CMF (BMF)	12	94 (91)

6.4.11 Synthesis of alkyl levulinates from different monohydric alcohols

A series of ALs were prepared by the alcoholysis of CMF and BMF in the presence of the $HClO_4$-SiO_2 catalyst. The reactions were carried out at 120 °C for 6 h in a glass pressure vessel using excess (ca. 10 mL) of the alcohol reagent and 4 wt% of the $HClO_4$-SiO_2 (0.828 mol% $HClO_4$) catalyst **(Table 6.7)**. When the preparation of BL from CMF was attempted in only slight excess (ca. 1.5 eq.) of 1-butanol, only 30% of BL was isolated with a noticeably high amount of humin formation. The result may be explained by the decomposition of CMF at relatively high acid concentrations. However, the use of excess 1-butanol (10 mL) provided BL in 97% yield from both CMF and BMF. ML was recovered in 89% yield starting from CMF, whereas BMF provided the same in 92% yield. Ethanolysis of CMF at 120 °C formed EL in a 90% yield. Under identical conditions, whereas BMF provided EL in 91% yield. The alcoholysis of CMF and BMF in 1-propanol provided PrL in 89% and 93% isolated yield, respectively. PL and hexyl levulinate (HL) formed in 90% and 91% respectively from CMF **(Entry 5&6)**. In all cases, the yield of AL was found to be slightly higher for BMF as a starting material when compared to CMF.

Table 6.7 Preparation of ALs from XMF using the $HClO_4$-SiO_2 catalyst

Entry	Substrate	Reaction conditions[a]	Product	Yield (%)[b]
1	CMF (BMF)	$HClO_4$-SiO_2 (0.828 mol%), 120 °C, 6 h, methanol (10 mL)	ML	89 (92)
2	CMF (BMF)	$HClO_4$-SiO_2 (0.828 mol%), 120 °C, 6 h, ethanol (10 mL)	EL	90 (91)

3	CMF (BMF)	$HClO_4$-SiO_2 (0.828 mol%), 120 °C, 6 h, 1-propanol (10 mL)	PrL	89 (93)
4	CMF (BMF)	$HClO_4$-SiO_2 (0.828 mol%), 120 °C, 6 h, 1-butanol (10 mL)	BL	97 (97)
5	CMF (BMF)	$HClO_4$-SiO_2 (0.828 mol%), 120 °C, 6 h, 1-pentanol (4 eq.)	PL	90 (92)
6	CMF (BMF)	$HClO_4$-SiO_2 (0.828 mol%), 120 °C, 6 h, 1-hexanol (4 eq.)	HL	91 (94)

[a] The reactions were performed in a sealed glass reactor, starting with 0.5 g of CMF or BMF. [b] Isolated yield.

We envisioned that the $HClO_4$-SiO_2 catalyst could also catalyze the alcoholysis of furfuryl alcohol (FA) into ALs **(Table 6.8)**. Therefore, the $HClO_4$-SiO_2 catalyst was employed as a catalyst under the optimized reaction conditions.

Table 6.8 Preparation of ALs from furfuryl alcohol using the $HClO_4$-SiO_2 catalyst

Entry[a]	Reaction conditions	Product	Yield (%)[b]
1	$HClO_4$-SiO_2 (0.550mol%), 120 °C, 6 h, methanol (5 mL)	ML	89
2	$HClO_4$-SiO_2(0.550 mol%), 120 °C, 6 h, ethanol (10 mL)	EL	84
3	$HClO_4$-SiO_2 (0.550 mol%), 120 °C, 6 h, 1-propanol (10 mL)	PrL	87
4	$HClO_4$-SiO_2 (0.550 mol%), 120 °C, 6 h, 1-butanol (10 mL)	BL	93

[a] The reactions were performed in a sealed glass reactor starting with 0.5 g of FA. [b] Isolated yield.

Under the optimized condition, the ethanolysis of FA provided EL in 84% yield. The alcoholysis of FA in 1-propanol and 1-butanol provided PrL and BL in 87% and 93% yields, respectively. However, the reaction of FA did not complete in methanol within 6 h at 120 °C. Interestingly, when the amount of methanol was decreased to 5 mL, the reaction completed, and ML was obtained in 89% yield. The observation may be explained by lowered acid concentration with a more dilute solution and more ether formation in methanol compared to alcohols of higher chain length.

6.5 CONCLUSIONS

In summary, a one-pot preparation of ALs in high isolated yields has been achieved from biomass-derived LA, XMF (X=Cl, Br), and furfuryl alcohol using Homogeneous and Heterogeneous Acid Catalysts.

- A series of ALs were produced from LA using commercially-available HPAs under homogeneous acid catalysis. PTA was found to be the most effective catalyst for the solvent-free and scalable preparation of ALs. After the reaction, the PTA catalyst was recovered conveniently by precipitation and reused up to three consecutive cycles without noticeable loss in mass or activity.
- One-Pot preparation of ALs by the alcoholysis of biomass-derived XMF (X=Cl, Br) and furfuryl alcohol was achieved using silica-supported perchloric acid ($HClO_4$-SiO_2) as an inexpensive heterogeneous acid catalyst. The selective and high-yielding process employed only 4 wt% of the $HClO_4$-SiO_2 catalyst.

CHAPTER 7

SUMMARY AND CONCLUSIONS

This chapter contains the summary and significant conclusions drawn from the present research study. It also includes a brief account of the scope of future work.

7.1 SUMMARY

- There has been significant research in the past three decades on the chemocatalytic conversion of lignocellulosic biomass into commercially-attractive renewable biofuels and chemicals.
- The present work focused on the catalytic transformation of carbohydrates into renewable chemical intermediates like HMF, CMF, BMF, and LA in high isolated yields and their synthetic upgrading into specialty chemicals like 5-(alkoxymethyl)furfural (AMF) and alkyl levulinate (AL).
- Although high-yielding production of CMF from biomass exists in the literature, the process requires a large volume of organic solvent, low loading of the carbohydrate substrate, and intermittent extraction of CMF from the reaction medium. However, a more commercially-attractive process would require less dependency on organic solvent with increased substrate loading in a true '*one-pot*' process without the obligation of intermittent extractions. The present research employed quaternary ammonium chloride as a phase transfer catalyst (PTC) for the transformation of sugars and carbohydrates to CMF in an HCl (35%)-DCE biphasic closed batch reactor. Among the various PTC examined, benzyltributylammonium chloride (BTBAC) noticeably improved the yield of CMF compared to the control reaction.
- BTBAC was used as a surface-active agent (SAA) for the direct conversion of biomass-derived carbohydrates into LA in azeotropic HCl (20.2% HCl). The reaction was optimized on the loading of carbohydrate, loading of BTBAC, reaction temperature, and duration of the reaction. Noticeably higher yields of LA were obtained compared to the control reactions (no BTBAC). The aq. HCl was recovered by distillation, and BTBAC was recovered by extraction and purified by column chromatography.
- A selective and scalable synthetic protocol was developed for the transformation of CMF and BMF into AMF, a promising fuel oxygenate. The HCl and HBr were recovered by a water wash. The side product like EL and

acetals were avoided by not allowing the acid concentration to build up during the work-up procedure. In the first strategy, lower alcohols (methanol to 1-butanol) were used as a solvent for the nucleophilic substitution reaction and completed within 3 h at moderate temperatures. In the second strategy, the equivalent amount of DIPEA was used as a base additive to provide AMFs in excellent yields using an only slight excess of the primary alcohols with longer alkyl chain or secondary alcohols.

- One-pot preparation of AL in high isolated yields was achieved by the alcoholysis of XMF (X=Cl, Br) or esterification of LA using homogeneous and heterogeneous catalysts. A series of ALs were prepared by Fischer esterification between LA and alkyl alcohols using commercially-available HPAs. After the reaction, the PTA catalyst was recovered conveniently by precipitation and reused up to three consecutive cycles without noticeable loss in mass or activity.
- One-pot preparation of ALs by the alcoholysis of biomass-derived CMF, BMF, and furfuryl alcohol was examined using various heterogeneous acid catalysts. Perchloric acid supported on silica gel ($HClO_4$-SiO_2) effectively catalyzed the alcoholysis of XMF and furfuryl alcohol into ALs. In this process, a series of ALs were prepared in high isolated yields from XMF and furfuryl alcohol using only 4 wt% of the $HClO_4$-SiO_2 catalyst.

7.2 CONCLUSIONS

The main objectives of this thesis were to develop a scalable and high-yielding synthesis of CMF and LA from biomass-derived carbohydrates and also to prepare value-added products from these renewable chemical building blocks. As discussed in CHAPTER 3 to CHAPTER 6, the objectives were fulfilled.

CMF has been produced in good isolated yields from biomass-derived carbohydrates within a closed aqueous HCl-1,2-dichloroethane biphasic reactor in the presence of benzyltributylammonium chloride (BTBAC) as a phase transfer catalyst (PTC). The solvent-economic, one-pot strategy afforded CMF in 73% isolated yield (90 °C, 3 h) from sucrose with a combined yield of 84% for CMF and LA. The process was optimized on temperature, duration, solvent, type, and loading of PTC. The use of BTBAC led to nearly a 10% increase in yield of CMF for all substrates when compared to control reactions. LA was also isolated in marginally higher yields in reactions using BTBAC compared to the control reactions. The humic matter was formed in noticeable lower quantities in reactions using BTBAC.

A one-pot production of LA from biomass-derived carbohydrates has been achieved in 20.2% aqueous hydrochloric acid within a batch-type reactor in the presence of BTBAC as a surface-active agent (SAA). The reactions provided a good isolated yield of LA even at high substrate loading (10 wt%) at relatively mild reaction conditions (120 °C, 3 h). BTBAC was found to be the most effective SAA that gave 8-17% more yield of LA from all the carbohydrates examined. Both LA and BTBAC were isolated from the aqueous reaction mixture by the distillative removal of aqueous hydrochloric acid or *via* solvent-solvent extraction.

A series of 5-(alkoxymethyl)furfurals (AMFs) have been synthesized in excellent isolated yields (>90%) by reacting biomass-derived CMF or BMF with monohydric alkyl alcohols (methanol to 1-butanol) at slightly elevated temperatures (RT-50 °C) and short reaction time (3 h). The modified work-up procedure minimizes side reactions while simplifying the isolation and purification of AMFs. Although higher primary alcohols like 1-pentanol and 1-hexanol and secondary alcohol like 2-propanol were found to be less reactive, use of *N*,*N*-diisopropylethylamine (DIPEA) as a base additive afforded AMFs in excellent yields within 6 h at 65 °C using an only slight excess of the alcohol (1.2 eq.) reagent.

The synthesis of a series of alkyl levulinates from biomass-derived 5-(halomethyl)furfural (X=Cl, Br) and furfuryl alcohol is reported using silica-supported perchloric acid ($HClO_4$-SiO_2) as a heterogeneous acid catalyst. The solvent-free, one-pot preparation afforded levulinate esters in excellent isolated yields (>84%). The reactions were performed at 120 °C for 6 h in a batch-type glass pressure reactor using only a slight excess of the alcohol reagent and 4 wt% of the $HClO_4$-SiO_2 catalyst (0.828 mol% $HClO_4$). Alkyl levulinates have also been produced in high isolated yields from LA using HPAs as homogeneous catalysts. The esterification reactions were conducted in a glass pressure reactor using only a slight excess of alcohol. The HPA catalyst was successfully recovered by precipitation and recycled for three consecutive cycles without significant loss of mass or activity.

7.3 SCOPE FOR FUTURE WORK

The present work demonstrates a scalable and high-yielding preparation of CMF and LA from biomass-derived carbohydrates in the presence of quaternary ammonium chloride as the surface-active agent (SAA). The SAA provided noticeably higher yields of CMF and LA under mild conditions compared to the control reactions (without SAA). Similarly, the effect of SAA on the production of 5-(hydroxymethyl)furfural (HMF) and furfural should be studied. The mechanistic details of the stabilization effect of SAA on CMF and LA should also be explored. The effect of SAA on the derivative chemistries of CMF and LA should also be studied. The synthesis of 5-(alkoxymethyl)furfural (AMF) from CMF using inexpensive inorganic bases such as coal-derived fly-ash should be investigated. A new generation of robust, selective, inexpensive, and eco-friendly catalysts should be developed to advance the derivative chemistries of biomass-derived renewable chemicals, including CMF and LA.

REFERENCES

Acharjee, T.C., and Lee, Y.Y. (2018). "Production of levulinic acid from glucose by dual solid-acid catalysts." *Environ. prog. sustain.*, 37(1), 471-480.

Adeleye, A.T., Louis, H., Akakuru, O.U., Joseph, I., Enudi, O.C. and Michael, D.P. (2019). "A Review on the conversion of levulinic acid and its esters to various useful chemicals." *AIMS Energy.*, 7(2), 165-185.

Ahmad, E., Alam, M.I., Pant, K. and Haider, M.A. (2016). "Catalytic and mechanistic insights into the production of ethyl levulinate from biorenewable feedstocks." *Green Chem.*, 18(18), 4804-4823.

Ahmed, M.M., Nasri, N.S. and Hamza, D.U. (2012). "Biomass as a renewable source of chemicals for industrial applications." *Int. J. Eng. Sci. Tech.*, 4(2), 721-730.

Al-Shaal, M.G., Ciptonugroho,W., Holzhäuser, F.J., Mensah, J.B., Hausoul, P.J. and Palkovits, R. (2015). "Catalytic upgrading of α-angelica lactone to levulinic acid esters under mild conditions over heterogeneous catalysts." *Catal. Sci.*, 5(12), 5168-5173.

Alam, M.I., De, S., Dutta, S. and Saha, B. (2012). "Solid-acid and ionic-liquid catalyzed one-pot transformation of biorenewable substrates into a platform chemical and a promising biofuel." *RSC Adv.*, 2(17), 6890-6896.

Alipour, S., Omidvarborna, H. and Kim, D.S. (2017). "A review on synthesis of alkoxymethyl furfural, a biofuel candidate." *Renew. Sust. Energ. Rev.*,71, 908-926.

Alonso, D.M., Bond, J.Q. and Dumesic, J.A. (2010). "Catalytic conversion of biomass to biofuels." *Green Chem.*, 12(9), 1493-1513.

Alonso, D.M., Wettstein, S.G. and Dumesic, J.A. (2013). "Gamma-valerolactone, a sustainable platform molecule derived from lignocellulosic biomass." *Green Chem.*, 15 (3), 584-595.

An, S., Song, D., Sun, Y., Zhang, Q., Zhang, P. and Guo, Y. (2018). "Conversion of furfuryl alcohol to levulinic acid in aqueous solution catalyzed by shell thickness-controlled arenesulfonic acid-functionalized ethyl-bridged organosilica hollow nanospheres." *ACS Sustain. Chem. Eng* ., 6 (3), 3113-3123.

Ansari, M.I., Hussain, M.K., Yadav, N., Gupta, P.K. and Hajela, K. (2012). "Silica supported perchloric acid catalyzed rapid N-formylation under solvent-free conditions." *Tetrahedron lett.*, 53(16), 2063-2065.

Antonetti, C., Licursi, D., Fulignati, S., Valentini, G. and Raspolli Galletti, A.M. (2016). "New frontiers in the catalytic synthesis of levulinic acid: from sugars to raw and waste biomass as starting feedstock." *Catalysts*, 6(12), 196.

Arslan, A., Gunduz, S. and Dogu, T. (2014). "Steam reforming of ethanol with zirconia incorporated mesoporous silicate supported catalysts." *Int. J. Hydrog. Energy.*, 39(32), 18264-18272.

Bai, F., Anderson, W. and Moo-Young, M. (2008). "Ethanol fermentation technologies from sugar and starch feedstocks." *Biotechnol. Adv.*, 26(1), 89-105.

Bai, Y., Wei, L., Yang, M., Chen, H., Holdren, S., Zhu, G., Tran, D.T., Yao, C., Sun, R. and Pan, Y. (2018). "Three-step cascade over a single catalyst: synthesis of 5-(ethoxymethyl) furfural from glucose over a hierarchical lamellar multi-functional zeolite catalyst." *J. Mater. Chem. A.*, 6(17), 7693-7705.

Balakrishnan, M., Sacia, E.R. and Bell, A.T. (2012). "Etherification and reductive etherification of 5-(hydroxymethyl) furfural: 5-(alkoxymethyl) furfurals and 2, 5-bis (alkoxymethyl) furans as potential bio-diesel candidates." *Green Chem.*, 14(6), 1626-1634.

Balat, M., Balat, H. and Öz, C. (2008). "Progress in bioethanol processing." *Prog. Energy Combust. Sci.*, 34(5), 551-573.

Bayu, A., Guan, G., Karnjanakom, S., Hao, X., Kusakabe, K. and Abudula, A. (2016). "Catalytic synthesis of levulinic acid and formic acid from glucose in choline chloride aqueous solution." *ChemistrySelect*, 1(2), 180-188.

Bhanumurthy, N.R., Das, S. and Bose, S. (2014). “Oil price shock, pass-through policy and its impact on India.” *Market, Regulations and Finance*, India studies in business and economics, R. Khasnabis and I. Chakraborty, eds., New Delhi: Springer India, 231–253.

Binder, J.B. and Raines, R.T. (2009). "Simple chemical transformation of lignocellulosic biomass into furans for fuels and chemicals." *J. Am. Chem. Soc.*, 131 (5), 1979-1985.

Bing, L., Zhang, Z. and Deng, K. (2012). "Efficient one-pot synthesis of 5-(ethoxymethyl) furfural from fructose catalyzed by a novel solid catalyst." *Ind. Eng. Chem. Res.*, 51(47), 15331-15336.

Bozell, J.J. and Petersen, G.R. (2010). "Technology development for the production of biobased products from biorefinery carbohydrates—the US Department of Energy’s “Top 10” revisited." *Green Chem.*, 12(4), 539-554.

Braden, D.J., Henao, C.A., Heltzel, J., Maravelias, C.C. and Dumesic, J.A. (2011). "Production of liquid hydrocarbon fuels by catalytic conversion of biomass-derived levulinic acid." *Green Chem.*, 13(7), 1755-1765.

Brasholz, M., Von Kaenel, K., Hornung, C.H., Saubern, S. and Tsanaktsidis, J. (2011). "Highly efficient dehydration of carbohydrates to 5-(chloromethyl) furfural (CMF), 5-(hydroxymethyl) furfural (HMF) and levulinic acid by biphasic continuous flow processing." *Green Chem.*, 13(5), 1114-1117.

Bredihhin, A., Mäeorg, U. and Vares, L. (2013). "Evaluation of carbohydrates and lignocellulosic biomass from different wood species as raw material for the synthesis of 5-bromomethyfurfural." *Carbohydr. Res.*, 375, 63-67.

Breeden, S., Clark, J., Farmer, T., Macquarrie, D., Meimoun, J., Nonne, Y. and Reid, J. (2013). "Microwave heating for rapid conversion of sugars and polysaccharides to 5-chloromethyl furfural." *Green Chem.*, 15(1), 72-75.

Brundtland, G.H. (1987). "Our common future Call for action." *Environ. Conserv.*, 14(4), 291-294.

Carriquiry, M.A., Du, X. and Timilsina, G.R. (2011). "Second generation biofuels: Economics and policies." *Energy Policy*, 39(7), 4222-4234.

Chakraborti, A.K. and Gulhane, R. (2003). "Perchloric acid adsorbed on silica gel as a new, highly efficient, and versatile catalyst for acetylation of phenols, thiols, alcohols, and amines." *Chem. Comm.*, (15), 1896-1897.

Chen, B., Xu, G., Chang, C., Zheng, Z., Wang, D., Zhang, S., Li, K. and Zou, C. (2019). "Efficient One-Pot Production of Biofuel 5-Ethoxymethylfurfural from Corn Stover: Optimization and Kinetics." *Energy Fuels*, 33(5), 4310-4321.

Chen, J., Zhao, G. and Chen, L. (2014). "Efficient production of 5-hydroxymethylfurfural and alkyl levulinate from biomass carbohydrate using ionic liquid-based polyoxometalate salts." *RSC Adv.*, 4(8), 4194-4202.

Chen, Z., Chen, Q., Yang, J., Lin, Q., Huang, M. and Song, G. (2012). "Preparation of 5-chloromethylfurfural as potential intermediate for biofuels using bagasses as raw material." *Tran. Chi. Soc. Agri. Eng.*, 28 (24), 214-219.

Cheng, H., and Wang, L. (2013). “Lignocelluloses feedstock biorefinery as petrorefinery substitutes.” *Biomass Now - Sustainable Growth and Use*, M. D. Matovic, ed., Intechopen, london, United Kingdom, 347-388.

Cheng, H. N., Gross, R. A., and Smith, P. B. (Eds.). (2015). *Green polymer chemistry: Biobased Materials and Biocatalysis*. ACS symposium series, Washington, DC: American Chemical Society.

Cherubini, F. (2010). "The biorefinery concept: using biomass instead of oil for producing energy and chemicals." *Energy Convers. Manag.*, 51(7), 1412-1421.

Chheda, J.N., Román-Leshkov, Y. and Dumesic, J.A. (2007). "Production of 5-hydroxymethylfurfural and furfural by dehydration of biomass-derived mono-and poly-saccharides." *Green Chem.*, 9(4), 342-350.

Christensen, E., Williams, A., Paul, S., Burton, S. and McCormick, R.L. (2011). "Properties and performance of levulinate esters as diesel blend components." *Energy & fuels*, 25(11), 5422-5428.

Cirujano, F., Corma, A. and Xamena, F.L. (2015). "Conversion of levulinic acid into chemicals: Synthesis of biomass derived levulinate esters over Zr-containing MOFs." *Chem. Eng.*, 124, 52-60.

Climent, M.J., Corma, A. and Iborra, S. (2014). "Conversion of biomass platform molecules into fuel additives and liquid hydrocarbon fuels." *Green Chem.*, 16(2), 516-547.

Corma, A., Iborra, S. and Velty, A. (2007). "Chemical routes for the transformation of biomass into chemicals." *Chem. Rew.*, 107(6), 2411-2502.

Dai, J., Liu, Z., Hu, Y., Liu, S., Chen, L., Qi, T., Yang, H., Zhu, L. and Hu, C. (2019). "Adjusting the acidity of sulfonated organocatalyst for the one-pot production of 5-ethoxymethylfurfural from fructose." *Catal. Sci.*, 9(2), 483-492.

Dalpozzo, R., Bartoli, G., Sambri, L. and Melchiorre, P. (2010). "Perchloric acid and its salts: very powerful catalysts in organic chemistry." *Chem. Rew.*, 110(6), 3501-3551.

Danon, B., Marcotullio, G. and de Jong, W. (2014). "Mechanistic and kinetic aspects of pentose dehydration towards furfural in aqueous media employing homogeneous catalysis." *Green Chem.*, 16(1), 39-54.

de Jong, E., Dam, M., Sipos, L. and Gruter, G.J. (2012). "*Furandicarboxylic acid (FDCA), a versatile building block for a very interesting class of polyesters"*. ACS Publications, 1-13.

de Jong, E. and Jungmeier, G. (2015). "Biorefinery concepts in comparison to petrochemical refineries." *Industrial Biorefineries & White Biotechnology*, Elsevier, 3-33.

Démolis, A., Essayem, N. and Rataboul, F. (2014). "Synthesis and applications of alkyl levulinates." *ACS Sustain. Chem. Eng* , 2(6), 1338-1352.

Dharne, S. and Bokade, V. (2011). "Esterification of levulinic acid to n-butyl levulinate over heteropolyacid supported on acid-treated clay." *J. Nat. Gas Chem.*, 20(1), 18-24.

Dias, M.O., Ensinas, A.V., Nebra, S.A., Maciel Filho, R., Rossell, C.E. and Maciel, M. R.W. (2009). "Production of bioethanol and other bio-based materials from sugarcane bagasse: integration to conventional bioethanol production process." *Chem. Eng. Res. Des.*, 87(9), 1206-1216.

Dincer, I. (2000). "Renewable energy and sustainable development: a crucial review." *Renew. Sust. Energ. Rev.*, 4(2), 157-175.

Duffield, J.A. and Collins, K.J. (2006). "Evolution of renewable energy policy." *Choices*, 21(316-2016-7289), 9-14.

Dugmore, T.I., Clark, J.H., Bustamante, J., Houghton, J.A. and Matharu, A.S. (2017). "*Valorisation of biowastes for the production of green materials using chemical methods*. Springer, 73-121.

Fenton, H.J.H. and Gostling, M. (1899). "XLI.Bromomethylfurfuraldehyde." *J. Chem. Soc.*,75, 423-433.

Fenton, H.J.H. and Gostling, M. (1901). "LXXXV.Derivatives of methylfurfural." *J. Chem. Soc.*, 79, 807-816.

Fenton, H.J.H. and Robinson, F. (1909). "CXLVIII.Homologues of furfuraldehyde." *J. Chem. Soc.*, 95, 1334-1340.

Fernandes, D., Rocha, A., Mai, E., Mota, C.J. and Da Silva, V.T. (2012). "Levulinic acid esterification with ethanol to ethyl levulinate production over solid acid catalysts." *Appl. catl. A.*, 425, 199-204.

Flannelly, T., Dooley, S. and Leahy, J. (2015). "Reaction pathway analysis of ethyl levulinate and 5-ethoxymethylfurfural from D-fructose acid hydrolysis in ethanol." *Energy & Fuels*, 29(11), 7554-7565.

Flannelly, T., Lopes, M., Kupiainen, L., Dooley, S. and Leahy, J. (2016). "Non-stoichiometric formation of formic and levulinic acids from the hydrolysis of biomass derived hexose carbohydrates." *RSC Adv.*, 6(7), 5797-5804.

Frumkin, H., Hess, J. and Vindigni, S. (2009). "Energy and public health: the challenge of peak petroleum." *Public Health Rep.*, 124(1), 5-19.

Gao, W., Li, Y., Xiang, Z., Chen, K., Yang, R. and Argyropoulos, D. (2013). "Efficient one-pot synthesis of 5-chloromethylfurfural (CMF) from carbohydrates in mild biphasic systems." *Molecules,* 18(7), 7675-7685.

Garcés, D., Díaz, E. and Ordóñez, S. (2017). "Aqueous phase conversion of hexoses into 5-hydroxymethylfurfural and levulinic acid in the presence of hydrochloric acid: mechanism and kinetics." *Ind. Eng. Chem. Res.*, 56(18), 5221-5230.

Geboers, J.A., Van de Vyver, S., Ooms, R., de Beeck, B.O., Jacobs, P.A. and Sels, B. F. (2011). "Chemocatalytic conversion of cellulose: opportunities, advances and pitfalls." *Catal. Sci.*, 1(5), 714-726.

Girisuta, B., Janssen, L. and Heeres, H. (2006). "A kinetic study on the decomposition of 5-hydroxymethylfurfural into levulinic acid." *Green Chem.*, 8(8), 701-709.

Gollakota, A., Kishore, N. and Gu, S. (2018). "A review on hydrothermal liquefaction of biomass." *Renew. Sust. Energ. Rev.*, 81, 1378-1392.

Grant, L. K. (2011). "Can we consume our way out of climate change? A call for analysis." *The Behavior Analyst*, 34(2), 245-266.

Guzmán, I., Heras, A., Güemez, M., Iriondo, A., Cambra, J.F. and Requies, J.S. (2016). "Levulinic acid production using solid-acid catalysis." *Ind. Eng. Chem. Res.*, 55(18), 5139-5144.

Hamada, K., Yoshihara, H. and Suzukamo, G. (1982). "An improved method for the conversion of saccharides into furfural derivatives." *Chem. Lett*, 11 (5), 617-618.

Hamada, K., Yoshihara, H. and Suzukamo, G. (2001). "Novel Synthetic Route to 2, 5-Disubstituted Furan Derivatives through Surface Active Agent-Catalysed Dehydration of D (-)-Fructose." *J. Oleo Sci.*, 50(6), 533-536.

Hamelinck, C.N., Van Hooijdonk, G. and Faaij, A.P. (2005). "Ethanol from lignocellulosic biomass: techno-economic performance in short-, middle-and long-term." *Biomass Bioenrg.*, 28(4), 384-410.

Hayes, D.J., Fitzpatrick, S., Hayes, M.H. and Ross, J.R. (2006). "The biofine process–production of levulinic acid, furfural, and formic acid from lignocellulosic feedstocks." *Bio. Indus. proc.* 1, 139-164.

Hegner, J., Pereira, K.C., DeBoef, B. and Lucht, B.L. (2010). "Conversion of cellulose to glucose and levulinic acid via solid-supported acid catalysis." *Tetrahedron lett.* , 51(17), 2356-2358.

Hibbert, H. and Hill, H.S. (1923). "Studies on Cellulose Chemistry II. The Action of Dry Hydrogen Bromide on Carbohydrates and Polysaccharides1, 2." *J. Am. Chem. Soc.*, 45(1), 176-182.

Hoekman, S.K., Broch, A., Robbins, C., Ceniceros, E. and Natarajan, M. (2012). "Review of biodiesel composition, properties, and specifications." *Renew. Sust. Energ. Rev.*, 16(1), 143-169.

Horvat, J., Klaić, B., Metelko, B. and Šunjić, V. (1985). "Mechanism of levulinic acid formation." *Tetrahedron lett.*, 26(17), 2111-2114.

Huang, Y.B., Yang, T., Lin, Y.T., Zhu, Y.Z., Li, L.C. and Pan, H. (2018). "Facile and high-yield synthesis of methyl levulinate from cellulose." *Green Chem.*, 20(6), 1323-1334.

Huber, G.W., Iborra, S. and Corma, A. (2006). "Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering." *Chem. Rew.*, 106(9), 4044-4098.

Hulea, V. (2018). "Toward platform chemicals from bio-based ethylene: heterogeneous catalysts and processes." *ACS Catals*, 8(4), 3263-3279.

Imhof, P., Dias, A.S. and de Jong, G.J.G. (2009). "Furanics: versatile molecules for biofuels and bulk chemicals applications." *Biofuels Technol*, 1(2), 11-17.

Iris, K. and Tsang, D.C. (2017). "Conversion of biomass to hydroxymethylfurfural: A review of catalytic systems and underlying mechanisms." *Bioresour. Technol.*, 238, 716-732.

Ismalaj, E., Strappaveccia, G., Ballerini, E., Elisei, F., Piermatti, O., Gelman, D. and Vaccaro, L. (2014). "γ-Valerolactone as a renewable dipolar aprotic solvent deriving from biomass degradation for the Hiyama reaction." *ACS Sustain.Chem. Eng.*, 2(10), 2461-2464.

James, O.O., Maity, S., Usman, L.A., Ajanaku, K.O., Ajani, O.O., Siyanbola, T.O., Sahu, S. and Chaubey, R. (2010). "Towards the conversion of carbohydrate biomass feedstocks to biofuels via hydroxylmethylfurfural." *Energy Environ Sci.*, 3(12), 1833-1850.

Jeong, G.T. and Park, D.H. (2010). "Production of sugars and levulinic acid from marine biomass Gelidium amansii." *Appl Biochem Biotechnol.*, 161(1-8), 41-52.

Joshi, H., Moser, B.R., Toler, J., Smith, W.F. and Walker, T. (2011). "Ethyl levulinate: A potential bio-based diluent for biodiesel which improves cold flow properties." *Biomass Bioenrg.*, 35(7), 3262-3266.

Kamm, B., Gruber, P.R. and Kamm, M. (2006)."*Biorefineries-industrial processes and products*. *Appl Biochem Biotechnol.*, 37(5), 1255-1285.

Kang, E.S., Hong, Y.W., Chae, D.W., Kim, B., Kim, B., Kim, Y.J., Cho, J.K. and Kim, Y.G. (2015). "From Lignocellulosic Biomass to Furans via 5-Acetoxymethylfurfural as an Alternative to 5-Hydroxymethylfurfural." *ChemSusChem*, 8(7), 1179-1188.

Kang, S. and Yu, J. (2018). "Maintenance of a highly active solid acid catalyst in sugar beet molasses for levulinic acid production." *Sugar tech*, 20(2), 182-193.

Karakhanov, E., Maksimov, A., Zolotukhina, A. and Vinokurov, V. (2018). "Oxidation of p-Xylene." *Russ. J. Appl. Chem.*, 91(5), 707-727.

Katsoulis, D.E. (1998). "A survey of applications of polyoxometalates." *Chem. Rew.*, 98(1), 359-388.

Katsuda, Y., Chikamoto, T., Ogami, H., Hirobe, H. and Kunishige, T. (1969). "Novel insecticidal chrysanthemic esters." *Agric. Biol. Chem.*, 33(9), 1361-1362.

Kenworthy, J.R. (2003). "Transport energy use and greenhouse gases in urban passenger transport systems: a study of 84 global cities."

Kesieme, U., Pazouki, K., Murphy, A. and Chrysanthou, A. (2019). "Biofuel as an alternative shipping fuel: technological, environmental and economic assessment." *Renew. Sustain. Energy.*, 3(4), 899-909.

Khan, M.S., Ahmed, I., Mutalib, I.B.A. and Bostum, A. (2015). "Role of Oxygenated Additives for Diesel Fuel Blend" A Short Review." *J. Appl. Sci.*, 15(4), 619-625.

Kobayashi, H., Ohta, H. and Fukuoka, A. (2012). "Conversion of lignocellulose into renewable chemicals by heterogeneous catalysis." *Catal. Sci.*, 2(5), 869-883.

Kohl, T., Bizet, B., Kevan, P., Sellwood, C., Tsanaktsidis, J. and Hornung, C. (2017). "Efficient synthesis of 5-(chloromethyl) furfural (CMF) from high fructose corn syrup (HFCS) using continuous flow processing." *React. Chem. Eng.*, 2(4), 541-549.

Kraus, G.A. and Guney, T. (2012). "A direct synthesis of 5-alkoxymethylfurfural ethers from fructose via sulfonic acid-functionalized ionic liquids." *Green Chem.*, 14(6), 1593-1596.

Kumar, A. and Sharma, S. (2011). "Potential non-edible oil resources as biodiesel feedstock: an Indian perspective." *Renew. Sust. Energ. Rev.*, 15(4), 1791-1800.

Kumar, A., Gautam, A. and Dutt, D. (2016). "Biotechnological transformation of lignocellulosic biomass in to industrial products: an overview." *Adv.Biosci. Biotechnol.*, 7(3), 149-168.

Kumar, P., Barrett, D.M., Delwiche, M.J. and Stroeve, P. (2009). "Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production." *Ind. Eng. Chem. Res.*, 48(8), 3713-3729.

Kumar, V.B., Pulidindi, I.N., Mishra, R.K. and Gedanken, A. (2016). "Ga modified zeolite based solid acid catalyst for levulinic acid production." *ChemistrySelect*, 1(18), 5952-5960.

Kumaravel, S., Thiripuranthagan, S., Radhakrishnan, R., Erusappan, E., Durai, M., Devarajan, A. and Mukannan, A. (2019). "Liquid Phase Esterification of Levulinic Acid into Ethyl Levulinate Over Sulphobenzylated Nanoporous Al-SBA-15 Catalyst." *J. Nanosci. Nanotechnol.*, 19(11), 6965-6977.

Kumari, N., Olesen, J.K., Pedersen, C.M. and Bols, M. (2011). "Synthesis of 5-bromomethylfurfural from cellulose as a potential intermediate for biofuel." *Eur. J. Org. Chem.*, (7), 1266-1270.

Kunkes, E.L., Simonetti, D.A., West, R.M., Serrano-Ruiz, J.C., Gärtner, C.A. and Dumesic, J.A. (2008). "Catalytic conversion of biomass to monofunctional hydrocarbons and targeted liquid-fuel classes." *Sci.*, 322(5900), 417-421.

Kuster, B.F. (1977). "The influence of water concentration on the dehydration of D-fructose." *Carbohydr. Res.*, 54(2), 177-183.

Kuwahara, Y., Fujitani, T. and Yamashita, H. (2014). "Esterification of levulinic acid with ethanol over sulfated mesoporous zirconosilicates: Influences of the preparation conditions on the structural properties and catalytic performances." *Catal. Today.*, 237, 18-28.

Lane, D.R., Mascal, M. and Stroeve, P. (2016). "Experimental studies towards optimization of the production of 5-(chloromethyl) furfural (CMF) from glucose in a two-phase reactor." *Renew. Energy*, 85, 994-1001.

Lanzafame, P., Temi, D., Perathoner, S., Centi, G., Macario, A., Aloise, A. and Giordano, G. (2011). "Etherification of 5-hydroxymethyl-2-furfural (HMF) with ethanol to biodiesel components using mesoporous solid acidic catalysts." *Catal. Today.*, 175(1), 435-441.

Laugel, C., Estrine, B., Le Bras, J., Hoffmann, N., Marinkovic, S. and Muzart, J. (2014). "NaBr/DMSO-Induced Synthesis of 2, 5-Diformylfuran from Fructose or 5-(Hydroxymethyl) furfural." *ChemCatChem*, 6(5), 1195-1198.

Le, K., Zuo, M., Song, X., Zeng, X., Tang, X., Sun, Y., Lei, T. and Lin, L. (2017). "An effective pathway for 5-brominemethylfurfural synthesis from biomass sugars in deep eutectic solvent." *J. Chem. Technol. Biotechnol*, 92(12), 2929-2933.

Lew, C.M., Rajabbeigi, N. and Tsapatsis, M. (2012). "One-pot synthesis of 5-(ethoxymethyl) furfural from glucose using Sn-BEA and Amberlyst catalysts." *Ind. Eng. Chem. Res.*, 51(14), 5364-5366.

Li, C., Xu, G., Wang, C., Ma, L., Qiao, Y., Zhang, Y. and Fu, Y. (2019). "One-pot chemocatalytic transformation of cellulose to ethanol over Ru-WO x/HZSM-5." *Green Chem.*, 21(9), 2234-2239.

Li, G., Liu, W., Ye, C., Li, X. and Si, C.L. (2018). "Chemocatalytic Conversion of Cellulose into Key Platform Chemicals." *Int. J. of Polymer Science*, 2018.

Li, H., Peng, L., Lin, L., Chen, K. and Zhang, H. (2013). "Synthesis, isolation and characterization of methyl levulinate from cellulose catalyzed by extremely low concentration acid." *Journal of Energy Chemistry*, 22(6), 895-901.

Li, H., Govind, K.S., Kotni, R., Shunmugavel, S., Riisager, A. and Yang, S. (2014). "Direct catalytic transformation of carbohydrates into 5-ethoxymethylfurfural with acid–base bifunctional hybrid nanospheres." *Energy Convers. Manag.*, 88, 1245-1251.

Li, H., Saravanamurugan, S., Yang, S. and Riisager, A. (2016). "Direct transformation of carbohydrates to the biofuel 5-ethoxymethylfurfural by solid acid catalysts." *Green Chem.*, 18(3), 726-734.

Li, Z., Otsuki, A.L. and Mascal, M. (2018). "Production of cellulosic gasoline via levulinic ester self-condensation." *Green Chem.*, 20(16), 3804-3808.

Liu, A., Liu, B., Wang, Y., Ren, R. and Zhang, Z. (2014). "Efficient one-pot synthesis of 5-ethoxymethylfurfural from fructose catalyzed by heteropolyacid supported on K-10 clay." *Fuel*, 117, 68-73.

Liu, B., Zhang, Z., Huang, K. and Fang, Z. (2013). "Efficient conversion of carbohydrates into 5-ethoxymethylfurfural in ethanol catalyzed by $AlCl_3$." *Fuel*, 113, 625-631.

Liu, C., Zhang, K., Liu, Y. and Wu, S. (2019). "Esterification of Levulinic Acid into Ethyl Levulinate Catalyzed by Sulfonated Bagasse-carbonized Solid Acid." *BioResources*, 14(1), 2186-2196.

Liu, J., Tang, Y. and Fua, X. (2015). "Efficient conversion of carbohydratesto ethoxymethylfurfural and levulinic acid ethyl ester under the catalysis of recyclable DMSO/Brønsted acids." *Starch-Stärke*, 67(9-10), 765-771.

Lu, L., Beihai, H., Runcang, S. and Ruofei, H. (2007). "High-value chemicals from lignocellulosic biomass." *Prog. Chem.*, 19(7-8), 1206-1216.

Luque, R. and Triantafyllidis, K. (2016). "Valorization of lignocellulosic biomass." *ChemCatChem*, 8(8), 1422-1423.

Ma, F. and Hanna, M.A. (1999). "Biodiesel production: a review." *Bioresour. Technol.*, 70(1), 1-15.

Maity, S.K. (2015). "Opportunities, recent trends and challenges of integrated biorefinery: Part I." *Renew. Sust. Energ. Rev.*, 43, 1427-1445.

Mal, S.S., Tröppner, O., Ivanović-Burmazović, I. and Burger, P. (2013). "Tetraalkylphosphonium decavanadates: synthesis, structures, and solution properties." *Eur. J. Inorg. Chem.,* (10-11), 1960-1967.

Maneffa, A., Priecel, P. and Lopez-Sanchez, J.A. (2016). "Biomass-Derived Renewable Aromatics: Selective Routes and Outlook for p-Xylene Commercialisation." *ChemSusChem*, 9(19), 2736-2748.

Mascal, M. and Nikitin, E.B. (2008). "Direct, High-yield conversion of cellulose into biofuel." *Angew. Chem., Int. Ed*, 47(41), 7924-7926.

Mascal, M. and Nikitin, E.B. (2009). "Towards the efficient, total glycan utilization of biomass." *ChemSusChem.*, 2(5), 423-426.

Mascal, M. and Dutta, S. (2011). "Synthesis of the natural herbicide δ-aminolevulinic acid from cellulose-derived 5-(chloromethyl) furfural." *Green Chem.*, 13(1), 40-41.

Mascal, M. and Dutta, S. (2014)."*Chemical-catalytic approaches to the production of furfurals and levulinates from biomass*." Springer, 41-83.

Mascal, M., Dutta, S. and Gandarias, I. (2014). "Hydrodeoxygenation of the angelica lactone dimer, a cellulose-based feedstock: simple, high-yield synthesis of branched C7–C10 gasoline-like hydrocarbons." *Angew. Chem., Int. Ed*, 53(7), 1854-1857.

Mascal, M. (2019). "5-(Chloromethyl) furfural (CMF): A Platform for Transforming Cellulose into Commercial Products." *ACS Sustain. Chem. Eng.*, 7(6), 5588-5601.

McKendry, P. (2002). "Energy production from biomass (part 2): conversion technologies." *Bioresour. Technol.*, 83(1), 47-54.

Melero, J.A., Iglesias, J. and Garcia, A. (2012). "Biomass as renewable feedstock in standard refinery units. Feasibility, opportunities and challenges." *Energy Environ Sci*, 5(6), 7393-7420.

Meller, E., Aviv, A., Aizenshtat, Z. and Sasson, Y. (2016). "Preparation of halogenated furfurals as intermediates in the carbohydrates to biofuel process." *RSC Adv.*, 6(42), 36069-36076.

Mellmer, M.A., Gallo, J.M. R., Martin Alonso, D. and Dumesic, J.A. (2015). "Selective production of levulinic acid from furfuryl alcohol in THF solvent systems over H-ZSM-5." *ACS Catals*, 5(6), 3354-3359.

Menegazzo, F., Ghedini, E. and Signoretto, M. (2018). "5-hydroxymethylfurfural (HMF) production from real biomasses." *Molecules*, 23(9), 2201.

Morales, G., Paniagua, M., Melero, J. and Iglesias, J. (2017). "Efficient production of 5-ethoxymethylfurfural from fructose by sulfonic mesostructured silica using DMSO as co-solvent." *Catal. Today.*, 279, 305-316.

Morone, A., Apte, M. and Pandey, R. (2015). "Levulinic acid production from renewable waste resources: Bottlenecks, potential remedies, advancements and applications." *Renew. Sust. Energ. Rev.*, 51, 548-565.

Mulik, N., Niphadkar, P. and Bokade, V. (2019). "Synergetic combination of $H_2Zr_1PW_{12}O_{40}$ and Sn-Beta as potential solid acid catalyst for direct one-step transformation of glucose to ethyl levulinate, a biofuel additive." *Environ. prog. sustain.*

Nakanishi, T. and Komiyama, R. (2006). "Supply and Demand Analysis on Petroleum Products and Crude Oils for Asia and the World." *IEEJ, August.*

Nandiwale, K.Y., Sonar, S.K., Niphadkar, P.S., Joshi, P.N., Deshpande, S.S., Patil, V. S. and Bokade, V.V. (2013). "Catalytic upgrading of renewable levulinic acid to ethyl levulinate biodiesel using dodecatungstophosphoric acid supported on desilicated H-ZSM-5 as catalyst." *Appl. catl. A.: General*, 460, 90-98.

O'Sullivan, A., Sheffrin, S.M. and Perez, S.J. (2008)."*Economics: principles, applications, and tools*." Pearson Education.

Özçimen, D. and İnan, B. (2015). "An overview of bioethanol production from algae." *Biofuels-Status and Perspective*, 141-162.

Pahwa-Gajjar, S. and Wakeford, J. (2013). "Oil Shock Vulnerabilities & Impacts: India Case Study."

Panwar, N., Kothari, R. and Tyagi, V. (2012). "Thermo chemical conversion of biomass–Eco friendly energy routes."*Renew. Sust. Energ. Rev.*, 16(4), 1801-1816.

Papageorgiou, G.Z., Tsanaktsis, V. and Bikiaris, D.N. (2014). "Synthesis of poly (ethylene furandicarboxylate) polyester using monomers derived from renewable resources: thermal behavior comparison with PET and PEN." *Phys. Chem. Chem. Phys.*, 16(17), 7946-7958.

Pasquale, G., Vázquez, P., Romanelli, G. and Baronetti, G. (2012). "Catalytic upgrading of levulinic acid to ethyl levulinate using reusable silica-included Wells-Dawson heteropolyacid as catalyst." *Catal.Comm.*, 18, 115-120.

Patil, C.R. and Rode, C.V. (2018). "Synthesis of diesel additives from fructose over PWA/SBA-15 catalyst." *Fuel*, 217, 38-44.

Patil, S.K., Heltzel, J. and Lund, C.R. (2012). "Comparison of structural features of humins formed catalytically from glucose, fructose, and 5-hydroxymethylfurfuraldehyde." *Energy & Fuels*, 26(8), 5281-5293.

Peng, L., Lin, L., Zhang, J., Shi, J. and Liu, S. (2011). "Solid acid catalyzed glucose conversion to ethyl levulinate." *Appl. catl. A.: General*, 397(1-2), 259-265.

Pileidis, F.D. and Titirici, M.M. (2016). "Levulinic acid biorefineries: new challenges for efficient utilization of biomass." *ChemSusChem*, 9(6), 562-582.

Ragauskas, A.J., Williams, C.K., Davison, B.H., Britovsek, G., Cairney, J., Eckert, C. A., Frederick, W.J., Hallett, J.P., Leak, D.J. and Liotta, C.L. (2006). "The path forward for biofuels and biomaterials." *science*, 311(5760), 484-489.

Ramli, N. A.S., Zaharudin, N.H. and Amin, N.A.S. (2017). "Esterification of renewable levulinic acid to levulinate esters using Amberlyst-15 as a solid acid catalyst." *Jurnal Teknologi*, 79(1).

Rao, M.N. and Reddy, B.S. (2007). "Variations in energy use by Indian households: an analysis of micro level data." *Energy*, 32(2), 143-153.

Rao, S. and Lingaiah, N. (2018). "One pot selective transformation of biomass derived chemicals towards alkyl levulinates over titanium exchanged heteropoly tungstate catalysts." *Catal. Today.*, 309, 269-275.

Reddy Yenumala, S. and Maity, S.K. (2012). "Thermodynamic evaluation of dry reforming of vegetable oils for production of synthesis gas." *J. Renew. Sustain. Energy.*, 4(4), 043120.

Ren, H., Zhou, Y. and Liu, L. (2013). "Selective conversion of cellulose to levulinic acid via microwave-assisted synthesis in ionic liquids." *Bioresour. Technol.*, 129, 616-619.

Ren, H., Girisuta, B., Zhou, Y. and Liu, L. (2015). "Selective and recyclable depolymerization of cellulose to levulinic acid catalyzed by acidic ionic liquid." *Carbohydr. Polym*, 117, 569-576.

Rinaldi, R. and Schüth, F. (2009). "Acid hydrolysis of cellulose as the entry point into biorefinery schemes." *ChemSusChem.*, 2(12), 1096-1107.

Ritchie, H. and Roser, M. (2017). "Fossil fuels." *Our World in Data*,

Román-Leshkov, Y., Chheda, J.N. and Dumesic, J.A. (2006). "Phase modifiers promote efficient production of hydroxymethylfurfural from fructose." *Science*, 312(5782), 1933-1937.

Rosatella, A.A., Simeonov, S.P., Frade, R.F. and Afonso, C.A. (2011). "5-Hydroxymethylfurfural (HMF) as a building block platform: Biological properties, synthesis and synthetic applications." *Green Chem.*, 13(4), 754-793.

Rubin, E.M. (2008). "Genomics of cellulosic biofuels." *Nature*, 454(7206), 841.

S Thombal, R. and H Jadhav, V. (2014). "Efficient conversion of carbohydrates to 5-hydroxymethylfurfural (HMF) using $ZrCl_4$ catalyst in nitromethane." *Biofuel Res. J.*, 1(3), 81-84.

Saeman, J.F. (1945). "Kinetics of wood saccharification-hydrolysis of cellulose and decomposition of sugars in dilute acid at high temperature." Ind. Eng., 37(1), 43-52.

Saha, B. and Abu-Omar, M.M. (2014). "Advances in 5-hydroxymethylfurfural production from biomass in biphasic solvents." *Green Chem.*, 16(1), 24-38.

Saha, B.C. (2003). "Hemicellulose bioconversion." *J Ind Microbiol*, 30(5), 279-291.

Sanchez, O.J. and Cardona, C.A. (2008). "Trends in biotechnological production of fuel ethanol from different feedstocks." *Bioresour. Technol.*, 99(13), 5270-5295.

Sanda, K., Rigal, L. and Gaset, A. (1992). "Optimisation of the synthesis of 5-chloromethyl-2-furancarboxaldehyde from D-fructose dehydration and in-situ chlorination of 5-hydroxymethyl-2-furancarboxaldehyde." *J. Chem. Technol. Biotechnol.*, 55(2), 139-145.

Sheldon, R.A. (2014). "Green and sustainable manufacture of chemicals from biomass: state of the art." *Green Chem.*, 16(3), 950-963.

Sheldon, R.A. (2016). "Green Chem., catalysis and valorization of waste biomass." *J. Mol. Catl. A-Chem.: Chemical*, 422, 3-12.

Sheldon, R.A. (2018). "The road to biorenewables: carbohydrates to commodity chemicals." *ACS Sustain. Chem. Eng.*, 6(4), 4464-4480.

Shen, F., Smith Jr, R. L., Li, L., Yan, L. and Qi, X. (2017). "Eco-friendly method for efficient conversion of cellulose into levulinic acid in pure water with cellulase-mimetic solid acid catalyst." *ACS Sustain. Chem. Eng.*, 5(3), 2421-2427.

Shen, Y., Sun, J.K., Yi, Y.X., Wang, B., Xu, F. and Sun, R.C. (2015). "One-pot synthesis of levulinic acid from cellulose in ionic liquids." *Bioresour. Technol.*, 192, 812-816.

Simonetti, D.A. and Dumesic, J.A. (2008). "Catalytic strategies for changing the energy content and achieving C-C coupling in biomass-derived oxygenated hydrocarbons." *ChemSusChem.*, 1(8-9), 725-733.

Song, D., An, S., Sun, Y. and Guo, Y. (2016). "Efficient conversion of levulinic acid or furfuryl alcohol into alkyl levulinates catalyzed by heteropoly acid and ZrO2 bifunctionalized organosilica nanotubes." *J. Catal*, 333, 184-199.

Sudarsanam, P., Zhong, R., Van den Bosch, S., Coman, S.M., Parvulescu, V.I. and Sels, B.F. (2018). "Functionalised heterogeneous catalysts for sustainable biomass valorisation." *Chem. Soc. Rev.*, 47(22), 8349-8402.

Szabolcs, Á., Molnár, M., Dibó, G. and Mika, L.T. (2013). "Microwave-assisted conversion of carbohydrates to levulinic acid: an essential step in biomass conversion." *Green Chem.*, 15(2), 439-445.

Szmant, H.H. and Chundury, D.D. (1981). "The preparation of 5-chloromethylfurfuraldehyde from high fructose corn syrup and other carbohydrates." *J. Chem. Technol. Biotechnol.*, 31(1), 205-212.

Tahvildari, K., Taghvaei, S. and Nozari, M. (2011). "The study of hydroxymethylfurfural as a basic reagent for liquid alkanes fuel manufacture from agricultural wastes." *Int. J.*, 2(1).

Thananatthanachon, T. and Rauchfuss, T.B. (2010). "Efficient production of the liquid fuel 2, 5-dimethylfuran from fructose using formic acid as a reagent." *Angew. Chem., Int. Ed*, 49(37), 6616-6618.

Van Putten, R.J., Van Der Waal, J.C., De Jong, E., Rasrendra, C.B., Heeres, H.J. and de Vries, J.G. (2013). "Hydroxymethylfurfural, a versatile platform chemical made from renewable resources." *Chem. Rew.*, 113(3), 1499-1597.

Verma, P., Stevanovic, S., Zare, A., Dwivedi, G., Chu Van, T., Davidson, M., Rainey, T., Brown, R.J. and Ristovski, Z.D. (2019). "An Overview of the Influence of Biodiesel, Alcohols, and Various Oxygenated Additives on the Particulate Matter Emissions from Diesel Engines." *Energies*, 12(10), 1987.

Viil, I., Bredihhin, A., Mäeorg, U. and Vares, L. (2014). "Preparation of potential biofuel 5-ethoxymethylfurfural and other 5-alkoxymethylfurfurals in the presence of oil shale ash." *RSC Adv.*, 4(11), 5689-5693.

Wang, H., Deng, T., Wang, Y., Cui, X., Qi, Y., Mu, X., Hou, X. and Zhu, Y. (2013). "Graphene oxide as a facile acid catalyst for the one-pot conversion of carbohydrates into 5-ethoxymethylfurfural." *Green Chem.*, 15(9), 2379-2383.

Wang, S.S. and Yang, G.Y. (2015). "Recent advances in polyoxometalate-catalyzed reactions." *Chem. Rew.*, 115(11), 4893-4962.

Wang, S., Zhang, Z., Liu, B. and Li, J. (2013). "Silica coated magnetic Fe_3O_4 nanoparticles supported phosphotungstic acid: a novel environmentally friendly catalyst for the synthesis of 5-ethoxymethylfurfural from 5-hydroxymethylfurfural and fructose." *Catal. Sci.*, 3(8), 2104-2112.

Wang, Z.W., Lei, T.Z., Liu, L., Zhu, J.I., He, X.F. and Li, Z.F. (2012). "Performance investigations of a diesel engine using ethyl levulinate-diesel blends." *BioResources*, 7 (4), 5972-5982.

Wang, Z. and Chen, Q. (2016). "Conversion of 5-hydroxymethylfurfural into 5-ethoxymethylfurfural and ethyl levulinate catalyzed by MOF-based heteropolyacid materials." *Green Chem.*, 18(21), 5884-5889.

Weiqi, W. and Shubin, W. (2017). "Experimental and kinetic study of glucose conversion to levulinic acid catalyzed by synergy of Lewis and Brønsted acids." *Chem. Eng.*, 307, 389-398.

Whetten, R. and Sederoff, R. (1995). "Lignin biosynthesis." *The plant cell*, 7(7), 1001.

Wu, F., Yang, R. and Yang, F. (2015). "Metal Chlorides as Effective Catalysts for the One-Pot Conversion of Lignocellulose into 5-Chloromethylfurfural (5-CMF)." *BioResources*, 10(2), 3293-3301.

Xin, H., Zhang, T., Li, W., Su, M., Li, S., Shao, Q. and Ma, L. (2017). "Dehydration of glucose to 5-hydroxymethylfurfural and 5-ethoxymethylfurfural by combining Lewis and Brønsted acid."*RSC Adv.*, 7(66), 41546-41551.

Yan, L., Yao, Q. and Fu, Y. (2017). "Conversion of levulinic acid and alkyl levulinates into biofuels and high-value chemicals." *Green Chem.*, 19(23), 5527-5547.

Yang, F. and Tang, J. (2019). "Catalytic Upgrading of Renewable Levulinic Acid to Levulinate Esters Using Perchloric Acid Decorated Nanoporous Silica Gels." *ChemistrySelect*, 4(4), 1403-1409.

Yang, J., Huang, W., Liu, Y. and Zhou, T. (2018). "Enhancing the conversion of ethyl levulinate to γ-valerolactone over Ru/UiO-66 by introducing sulfonic groups into the framework." *RSC Adv.*, 8(30), 16611-16618.

Yang, J., Li, G., Zhang, L. and Zhang, S. (2018). "Efficient production of n-butyl levulinate fuel additive from levulinic acid using amorphous carbon enriched with oxygenated groups." *Catalysts*, 8(1), 14.

Yang, Y., Abu-Omar, M.M. and Hu, C. (2012). "Heteropolyacid catalyzed conversion of fructose, sucrose, and inulin to 5-ethoxymethylfurfural, a liquid biofuel candidate." *Appl.*, 99, 80-84.

Yang, Y., Hu, C. and Abu-Omar, M.M. (2012). "Conversion of glucose into furans in the presence of AlCl3 in an ethanol–water solvent system." *Bioresour. Technol.*, 116, 190-194.

Yi, X., Al-Shaal, M.G., Ciptonugroho, W., Delidovich, I., Wang, X. and Palkovits, R. (2017). "Synthesis of butyl levulinate based on α-angelica lactone in the presence of easily separable heteropoly acid catalysts." *ChemSusChem*, 10(7), 1494-1500.

Young, G., Nippen, F., Titterbrandt, S. and Cooney, M.J. (2011). "Direct transesterification of biomass using an ionic liquid co-solvent system." *Biofuels*, 2(3), 261-266.

Yu, F., Zhong, R., Chong, H., Smet, M., Dehaen, W. and Sels, B.F. (2017). "Fast catalytic conversion of recalcitrant cellulose into alkyl levulinates and levulinic acid in the presence of soluble and recoverable sulfonated hyperbranched poly (arylene oxindole) s." *Green Chem.*, 19(1), 153-163.

Zhang, X., Eren, N.M., Kreke, T., Mosier, N.S., Engelberth, A.S. and Kilaz, G. (2017). "Concentrated HCl catalyzed 5-(chloromethyl) furfural production from corn stover of varying particle sizes." *BioEnergy Res.*, 10(4), 1018-1024.

Zhang, Y., Chen, X., Lyu, X., Zhao, G., Zhao, T., Han, L. and Xiao, W. (2019). "Aluminum phosphotungstate as a promising bifunctional catalyst for biomass carbohydrate transformation to methyl levulinate under mild conditions." *J. Clean. Prod.*, 215, 712-720.

Zhang, Z., Wang, Y., Fang, Z. and Liu, B. (2014). "Synthesis of 5-ethoxymethylfurfural from fructose and inulin catalyzed by a magnetically recoverable acid catalyst." *ChemPlusChem*, 79(2), 233-240.

Zhang, Z. (2016). "Synthesis of γ-Valerolactone from Carbohydrates and its Applications." *ChemSusChem*, 9(2), 156-171.

Zhao, G., Liu, M., Xia, X., Li, L. and Xu, B. (2019). "Conversion of Furfuryl Alcohol into Ethyl Levulinate over Glucose-Derived Carbon-Based Solid Acid in Ethanol." *Molecules*, 24(10), 1881.

Zhao, S., Xu, G., Chang, C., Fang, S., Liu, Z. and Du, F. (2015). "Direct conversion of carbohydrates into ethyl levulinate with potassium phosphotungstate as an efficient catalyst." *Catalysts*, 5(4), 1897-1910.

Zhao, S., Xu, G., Chang, J., Chang, C., Bai, J., Fang, S. and Liu, Z. (2015). "Direct production of ethyl levulinate from carbohydrates catalyzed by H-ZSM-5 supported phosphotungstic acid." *BioResources*, 10(2), 2223-2234.

Zheng, X., Zhi, Z., Gu, X., Li, X., Zhang, R. and Lu, X. (2017). "Kinetic study of levulinic acid production from corn stalk at mild temperature using $FeCl_3$ as catalyst." *Fuel*, 187, 261-267.

Zuo, M., Li, Z., Jiang, Y., Tang, X., Zeng, X., Sun, Y. and Lin, L. (2016). "Green catalytic conversion of bio-based sugars to 5-chloromethyl furfural in deep eutectic solvent, catalyzed by metal chlorides." *RSC Adv.*, 6(32), 27004-27007.

LIST OF PUBLICATIONS

Papers published/communicated in international journals

1. Sharath Bandibairanahalli Onkarappa and Saikat Dutta (2019). "Phase transfer catalyst assisted the one-pot synthesis of 5-(chloromethyl)furfural from biomass-derived carbohydrates in a biphasic batch reactor". ***ChemistrySelect***, 4, 7502-7506.

2. Sharath Bandibairanahalli Onkarappa and Saikat Dutta (2019). "High-Yielding Synthesis of 5-(alkoxymethyl)furfurals from Biomass-Derived 5-(halomethyl)furfural (X=Cl, Br)". ***ChemistrySelect***, *4*(19), 5540-5543.

3. Sharath Bandibairanahalli Onkarappa, Manjunath Javoor, Sib Sankar Mal and Saikat Dutta (2019). "Efficient and Scalable Production of Alkyl Levulinates from Cellulose-Derived Levulinic Acid Using Heteropolyacid Catalyst". ***ChemistrySelect***, *4*(8), 2501-2504.

4. Sharath, B. O., Tiwari, R., Mal, S. S., & Dutta, S. (2019). "Straightforward synthesis of calcium levulinate from biomass-derived levulinic acid and calcium carbonate in egg-shells". ***Materials Today: Proceedings***, *17*, 77-84.

5. Sharath Bandibairanahalli Onkarappa, Navya Subray Bhat, Devaraj Parashuram and Saikat Dutta (2019). "Catalytic conversion of biomass-derived carbohydrates into levulinic acid assisted by a cationic surface-active agent". ***ChemistrySelect,*** 4(44), 13021-13024.

6. Sharath Bandibairanahalli Onkarappa, Navya Subray Bhat and Saikat Dutta. (2020). "Preparation of Alkyl Levulinates from Biomass-Derived Furfuryl Alcohol and 5-(Halomethyl)furfural (X=Cl, Br) Using Silica Supported Perchloric Acid ($HClO_4$-SiO_2) Catalyst". **(Accepted in Biomass Conversion and Biorefinery).**

7. Efficient production of furanics and levulinic acid from carbohydrates using quaternary ammonium salts as an additive (**C.000738-Indian Patent**)

8. Tiwari, R., Rahman, A., Bhat, N. S., Onkarappa, S. B., Mal, S. S., & Dutta, S. (2019). Efficient Preparation of Alkyl Benzoates by Heteropolyacid-Catalysed Esterification of Benzoic Acid under Solvent-Free Condition. ***ChemistrySelect***, *4*(31), 9119-9123.

Papers presented in national/international conferences

1. Presented Oral presentation on a research paper titled “One-pot, two-step synthesis of 2-furanoates from biomass-derived furfural using *tert*-butyl hypochlorite as a green oxidant” at National Conference on Emerging Trends in Science and Engineering (NCETSE-2017), 23rd & 24th February 2017, Shri Madhwa Vadiraja Institute of Technology and Management Bantakal, Udupi.

2. Presented Poster presentation on a research paper titled “Scalable synthesis of calcium levulinate for the production of Levulinic biofuels” at International Conference on Emerging Trends in Chemical Sciences-2017, 14-16 September 2017, Department of Chemistry, Manipal Institute of Technology, Manipal.

3. Presented Oral presentation on a research paper titled “Straightforward synthesis of calcium levulinate from biomass-derived Levulinic acid and calcium carbonate in egg-shells” at International Conference on Advanced Materials, Energy and Environmental Sustainability (ICAMEES-2018),14th & 15th December 2018, University of Petroleum and Energy Studies, Dehradun.

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- Ph.D. in Chemistry under the guidance of Dr. Saikat Dutta, Assistant professor, Department of chemistry, National Institute of Technology Karnataka (NITK), Surathkal, Mangalore, Karnataka, India (2016-2019)

Work Experience:

- Worked as Junior Research Fellow (JRF) and Senior Research Fellow (SRF) under DST-SERB sponsored project entitled “Renewable synthesis of hydrocarbon fuels and specialty chemicals from cellulose-derived angelica lactone” under the guidance of Dr. Saikat Dutta for three years.

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- Qualified CSIR-NET (AIR 28) in the year 2015.
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2. Sharath Bandibairanahalli Onkarappa and Saikat Dutta (2019) "High-Yielding Synthesis of 5-(alkoxymethyl)furfurals from Biomass-Derived 5-(halomethyl)furfural (X=Cl, Br)". ***ChemistrySelect***, *4*(19), 5540-5543.

3. Sharath Bandibairanahalli Onkarappa, Manjunath Javoor, Sib Sankar Mal and Saikat Dutta (2019) "Efficient and Scalable Production of Alkyl Levulinates from Cellulose-Derived Levulinic Acid Using Heteropolyacid Catalyst". ***ChemistrySelect***, *4*(8), 2501-2504.

4. Sharath, B. O., Tiwari, R., Mal, S. S., & Dutta, S. (2019). "Straightforward synthesis of calcium levulinate from biomass-derived levulinic acid and calcium carbonate in egg-shells". ***Materials Today: Proceedings***, *17*, 77-84.

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