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Conversion of Glucose into 5-hydroxymethylfurfural using zeolitic catalysts in water/acetone as solvent

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This is to certify that the thesis prepared by Destaw Engidaw entitled: Conversion of Glucose into HMF using zeolitic catalysts in water/acetone as solvent and submitted in partial fulfillment of the requirements for the Degree of Master of Science (Inorganic chemistry) complies with the regulation of the university and meets the accepted standards with respect to originality and quality.

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ABSTRACT

Production of 5-hydroxymethylfurfural, which is an important bio-resource intermediate, from glucose was examined in water/acetone solvent system, synthetic and modified mordenites and SAPO-5 materials as catalysts. The treatment of glucose at 100 ^{o}C with mordenite and at 120 ^{o}C with SAPO-5 materials gives limited amount of conversion. Modified mordenite at100 ^{o}C and 48h gave 28.41% and the SAPO-5 materials: 1.5T, which have a number of Bronsted acid sites but weaker in strength gave 13.66% of conversion while that of 1.5B which has a stronger Bronsted acidities gave 18% at 120 ^{o}C and 24 h in monophasic systems. In the case of biphasic system, a yield of 7.38 % at 6 h was obtained using synthetic Mordenite at 150 ^{o}C. Despite the efforts, the system is not yet optimized.

Key words: glucose, 5-hydroxymethylfurfural, water, mordenite, silicoaluminophosphate

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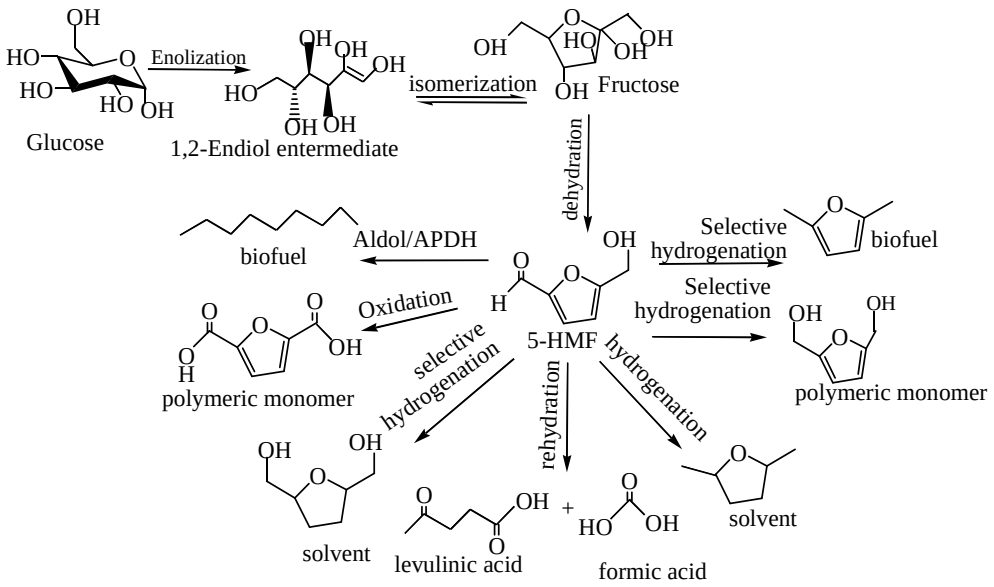
List of symbols and abbreviations

5-HMF	5-Hydroxymethylfurfural
ILs	Ionic liquids
DMSO	Dimethylsulfoxide
MIBK	Methylisobutylketone
Å	Angstrom
AlPOs	Aluminiumphosphates
SM1	Substitution mechanism one
SM2	Substitution mechanism two
SM3	Substitution mechanism three
SDAs	Structure directing agents
TEA	Triethylamine
BP	Benzylpyrollidine
NMR	Nuclear magnetic resonance
^{1}H NMR	Proton nuclear magnetic resonance
^{13}C NMR	Carbon-13 nuclear magnetic resonance
h	Hour
$CDCl_3$	Deuterated chloroform
s	Singlet
d	doublet
TGA	Thermal gravimetric Analysis

1. INTRODUCTION

The fast consumption and depletion of fossil fuels (petroleum, coal and natural gas), increasing demand of energy and the current issue of global warming are the major concerns nowadays. A major question we need to raise is how to change our dependence on non-renewable energy sources. Scientists give attention to overcome these major problems to find a solution. Reducing the reliance on non-renewable fossil fuels and developing the utilization of renewable feedstock is an alternative way for the sustainable contribution of energy.

Biomass, which possesses large amounts of stored chemical energy, could be transformed to value added chemicals that give little or no harmful side products which address the critical issue for greener alternatives to fossil fuels [1]. Carbohydrates are the major portion of the world's renewable biomass [2], which are precursor chemicals for the synthesis of a large number of substances such as liquid alkanes (C_3-C_{15}), furfural and 5-hydroxymethyl-2-furaldehyde, levulinic acid, etc. in different methods [3]. 5-hydroxymethylfurfural has been recognized as a versatile platform chemical for the production of other chemicals, pharmaceuticals, polymeric materials and biofuels (scheme 1) [4].



Scheme 1 Synthesis of HMF and its further derivatization in to important chemicals [5]

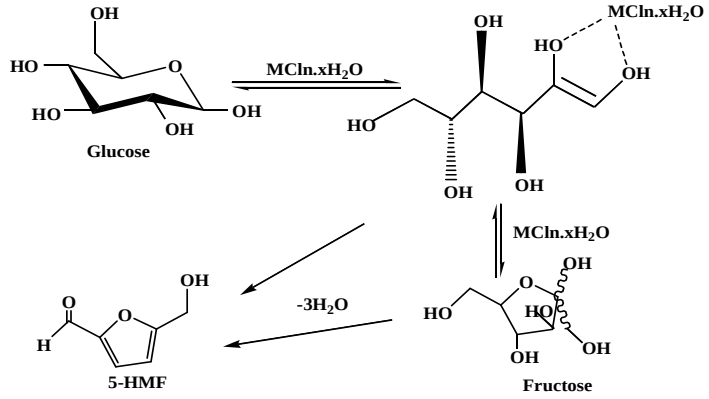
5-HMF and its derivatives levulinic acid, 2,5-bis(hydoxymethyl)-furan (2,5-BHF), 2,5-diformylfuran (2,5-DFF) and 2,5-furandicarboxylic acid (2,5-FDCA) were identified early as very promising chemical intermediates obtained by the catalytic conversion of carbohydrates based on C_6 units (hexoses) (scheme 1) [6].

The key matter is how to synthesize this versatile and platform compound from the renewable biomass feedstock that are locally accessible and possessing low carbon emissions.

1.1. Mechanism of hexose dehydration

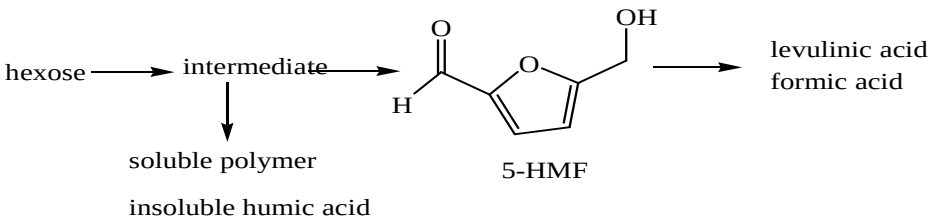
5-HMF can be obtained by dehydration of fructose in the presence of soluble or solid acid catalysts or from glucose or even polysaccharides by more complex catalytic systems and reaction media. Hence its synthesis is based on the triple dehydration of C_6-sugars (i.e., hexoses). The formation of HMF is proposed to take place through the dehydration of a 5 member monosaccharide ring, fructose which contains 21.5% of furanose tautomers in aqueous solution more efficiently converted to HMF than glucose which contains 1% of furanose tautomers in aqueous solutions which is more difficult to dehydrate. As a result, a catalytic system that efficiently converts glucose (which is more directly abundant and less expensive than fructose) to HMF in water has yet to be developed.

Although glucose can be converted with low yields to HMF using Brønsted acids, the yield to HMF can be increased notably, if glucose is first isomerized to fructose before the acid catalyzed dehydration, and fructose is then dehydrated to HMF [2, 7]. In 2007, Zhang and co-workers reported that chromium chloride salts catalyze glucose-fructose isomerization in ionic liquids. This enables the rapid conversion of glucose into HMF in the absence of aqueous acid. Thus HMF could be isolated in high yield without subsequent hydrolytic fragmentation to levulinic acid and formic acid [8, 9].



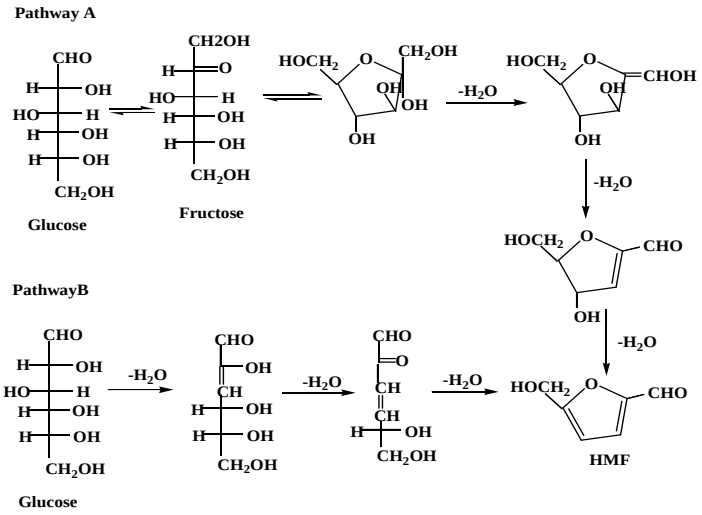
Scheme 2 Transition-metal-catalyzed isomerization of glucose into fructose and subsequent dehydration to HMF

The synthesis of HMF from monosaccharides is not an easy process, because it requires the loss of three water molecules, which is catalyzed by acids. This dehydration method is a very complex process due to the possibility of side-reactions; the decomposition to levulinic and formic acids and the polymerisation to humic acids are the most important factors decreasing the yield of HMF [3, 4 and 10].



Scheme 3 Dehydration of hexose to HMF [3]

The mechanism for fructose dehydration reaction is not clear, and two different pathways have been proposed for the formation of HMF, either via acyclic compounds or cyclic compounds (Scheme 4) [3, 4].



Scheme 4 Mechanism of hexose dehydration into 5-HMF [4]

Glucose reactivity is lower than fructose, due to the much lower abundance of acyclic glucose compared to acyclic fructose. Glucose can form a very stable ring structure, so the enolisation rate in solution is lower than fructose, which forms less stable ring structures. Since enolisation is the rate-determining step for HMF formation, fructose will react much faster than glucose. On the other hand, fructose forms equilibrium mixtures of difructose and dianhydrides, and thus the most reactive groups are internally blocked, forming smaller amounts of by-products. Glucose forms true oligosaccharides which still contain reactive reducing groups, resulting in a greater risk of cross-polymerization with reactive intermediates and HMF.

1.2. Solvents for the production of HMF

The dehydration of hexose to HMF has been conducted in water, in aprotic organic solvents and ionic liquids, and also in biphasic systems in the presence of acid catalysts [11, 12].

1.2.1. Non-aqueous solvents

Solvents such as dimethylsulfoxide (DMSO), N, N-dimethylacetamide (DMA), N, N-dimethylformamide (DMF), n-butanol, acetone, dioxane, polyglycol ether have been reported as the reaction medium in the dehydration of hexose to HMF [2, 3]. However, the use of these solvents has a drawback due to the poor solubility of hexose and problem

of separation of HMF from the reaction medium. The solubility problems can be overcome by the application of mixed-solvent (water-organic) systems. In this work, we have tried acetone/water mixtures using SAPOs and mordenite as catalysts in order to compare with our previous work on Ionic Liquids.

1.2.2. Ionic liquids as solvents

Ionic liquids (ILs) are normally defined as salts that are liquid below 100 ^{o}C that consists of large organic cations and smaller inorganic anions or vice versa and exhibit unique characteristics, such as a negligible vapor pressure, non-flammability, high thermo stability, and close to infinite structural variation. Chloride based ILs have an exceptionally high capacity for dissolving carbohydrates since the extensive hydrogen bonding network that constitutes the structure of the solid carbohydrate is disrupted [13-16]. Ionic liquids are considered as environmentally friendly substitute for volatile organic solvents, not only because of their low vapor pressures, but, more importantly, also because of their ability to act as catalysts [16-18]. Zhao et al. [8], first reported HMF yields of 68-70 % from glucose in the ionic liquid 1-ethyl-3-methyl-imidazolium chloride [EMIM] Cl using $CrCl_2$ as the Lewis acid catalyst. In subsequent studies with ionic liquids, HMF was produced from glucose with yields higher than 90 % [19]. High yield of HMF has been achieved in ionic liquids starting from fructose or glucose. However, ionic liquids are not yet suitable for large scale applications due to their high cost and deactivation by small amounts of water [15, 19 and 20]. But not only their cost, the use of ILs as solvents during the conversion of glucose to HMF by using zeolites as catalysts may deactivate the catalytic activity of the zeolite because they are bulkier molecules and hence stack into the pores of the zeolite which cannot easily diffused. As a result deactivation of the catalyst activity may reduced the yield of HMF, that is why we are preferring water as a solvent for conversion of glucose to HMF.

1.2.3. Water as solvent

Dehydration of fructose in pure water using solid and mineral acids is generally non-selective, about 6% and HMF yields < 20% due to the degradation of HMF via rehydration reactions [3, 21]. The difficulties for a selective 5-HMF synthesis in water is due to the uncontrolled re-hydration of 5-HMF to levulinic and formic acids. In addition

intermediates or the 5-HMF may polymerize to produce oligomers, called humins, which are more or less soluble in water [22]. To solve the problems of the low 5-HMF selectivity in the water medium, the following approaches were reported:

1. In situ extraction of 5-HMF from the reaction media to avoid its successive transformation by using a 5-HMF extractive solvent, immiscible in water.
2. Perform the reaction in organic/aqueous media or in pure organic solvent like DMSO**.**
3. Ionic liquids are being increasingly investigated to synthesize 5-HMF [12, 22].

1.2.4. Biphasic system

A biphasic reactor system consists of an aqueous solution and water immiscible organic solution that continuously extract the HMF from the aqueous phase as it is formed and is thereby protected against degradation reactions [3, 7, 21]. In the literature many extractive organic solvents have been mentioned such as 1-butanol, MIBK, dichloromethane (DCM), ethyl acetate, diethylether and THF [3, 21-25]. However, most extracting solvents used show poor partitioning of HMF into the organic phase. Recently it has been reported that the addition of a salt (e.g., NaCl) to the aqueous phase improves the partitioning of HMF into the extracting phase by means of the ‘‘salting-out effect’’ and leads to increased HMF yields without the use of high-boiling-point solvents, Roman-Leshkov et al. [21], and Hansen et al. [25].

Partitioning of organic molecules and water by the principle of “salting-out effect” means that water miscible organic compounds can be separated into two parts; the aqueous phase and the organic phase due to the strong interaction between water dipoles and the ions of salt. As a result, water molecules will be crystallized or sink out by leaving the organic phase in another part. Even the gap between immiscible organic compounds and water could also be more efficiently maximize by using salts like NaCl and KCl. As a result, biphasic rector systems are applied in the conversion of glucose to HMF using Mordenite as catalyst, water/acetone as reaction media and ethyl acetate as extracting solvent.

1.3. Catalysts for the dehydration of glucose to 5-HMF

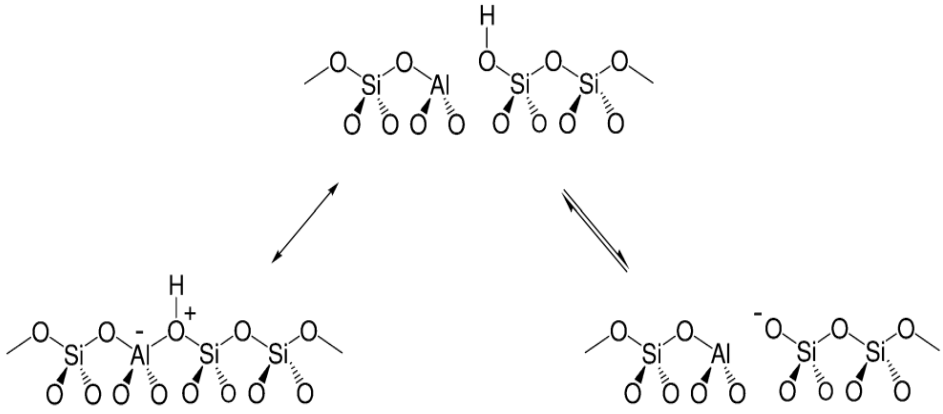
Different catalytic systems could be used for the conversion of hexoses to HMF: consisting of homogenous acids; such as mineral acids like HCl, H_2SO_4, H_3PO_4 and

organic acids such as oxalic acid, levulinic acid and maleic acid and heterogeneous acids such as strong acid cation exchange resins, supported heteropolyacids, metal oxides and zeolites and zeotypes.

Catalytic application of homogenous acid has serious drawbacks in terms of separation, recycling and material corrosion, while heterogeneous acids can be recycled and have high selectivity to the desired compound. However, zeolites and mesoporous materials are promising solid acid catalysts because of their specific structure of the pores and cages, and particular surface chemistry.

1.3.1. Zeolites as catalysts

Zeolites are natural or synthetic crystalline, porous aluminosilicates, minerals of which framework are composed by the assembling of SiO_4 and AlO_4^- tetrahedral units. They are mainly used in ion exchange, adsorptive separations and heterogeneous catalysis. The achievement of the catalysis activity is attributed to the presence of strong acid sites on the frameworks with well-defined microporous structures that are responsible for the shape-selectivity (pore diameter <15Å) [26, 27]. The Brønsted acid strength of the H-form is related to the Si/Al ratio. The number of proton donor hydroxyl groups corresponds to the number of aluminum atoms present in the structure. The more isolated this silanol species, the stronger the acid, i.e. the acid strength increases with decreasing aluminum content or increasing Si/Al ratio, but note that complete replacement of aluminum gives a material with lower acidity [28].

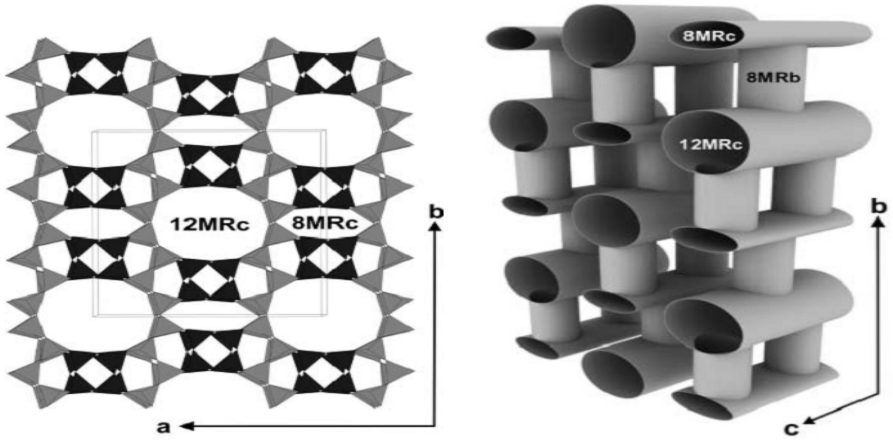


Scheme 5 Acid form of zeolites

The wide range of pore sizes available, coupled with their tunable acidity, gives the zeolites with unique properties as tailor-made acid catalysts. These important features of zeolites and also zeotypes may be generalized as: (I) regular microenvironment and uniform internal structure, (II) large internal surface area, (III) pores of molecular dimensions (shape selectivity), (IV) control of pore size and shape by choice of template and/or post synthesis modification,(V) control of pore hydrophobicity/hydrophilicity, (VI) control of acidity by adjusting constitution (Si/Al ratio), ion exchange or post-synthesis modification, (VII) framework substitution by transition elements and (VIII) the presence of strong electric fields within the confined space of the channels and cavities can serve to activate substrate molecules [28].

Zeolites have several advantages for the dehydration of glucose or fructose: They are more selective than ion exchange resins in water as the solvent; they can work at high temperatures, thus favoring the formation of 5-HMF as compared to its decomposition; they are capable of adsorbing organic acids partly responsible for the further degradation of 5-HMF and they are easily regenerated by thermal process. However, in catalytic reaction of bulky molecules, the sole presence of micropores inhibits simplistic mass transfer to and from the active sites, often limiting the catalytic applications [29].

Mordenite, with an ideal composition of $Na_8Al_8Si_{40}O_{96}.24H_2O$, is one of the most siliceous natural zeolite having an orthorhombic unit cell of topological space-group symmetry C*mcm* (a = 18.13 Å, b = 20.5 Å, c = 7.52 Å). The structure of mordenite can be describe as composed of edge-sharing five membered rings of tetrahedral (secondary building unit 5-1) forming chains along c axis. However, the mordenite framework can also be more comprehensibly envisioned as composed of puckered sheets parallel to (100), made up of six membered rings of tetrahedral. These sheets are interlinked by four membered rings (fig. 1) such that large, ellipsoidal twelve membered (12MRc: aperture 7 × 6.5 Å) and strongly compressed eight membered rings (8MRc: aperture 5.7 × 2.6 Å) define channels parallel to c axis. Another set of compressed eight membered rings (8MRc: aperture 3.4 × 4.8 Å) connects the wide channels with strongly compressed channels parallel to b [30, 31].



(A) (B)

Figure 1 (A) Tetrahedral frame work structure of mordenite with unit cell outlines, (B) Plumbing system in mordenite accessible for extra framework- cation and molecule diffusion [30].

Even if mordenite is a large pore zeolite, it is highly sensitive to pore blocking due to its pseudo monodimensional pore system, which was responsible for the diffusion of large extra framework ions and molecules [28, 30, 31]. From fig.1 (B) above it is noticed that there is no straight connection between adjacent 12MRc tubes. The linking 8MRb tubes are staggered at the join with the strongly compressed 8MRc tubes. Thus for diffusion of large molecules the structure of mordenite offers only one dimensional passageways.

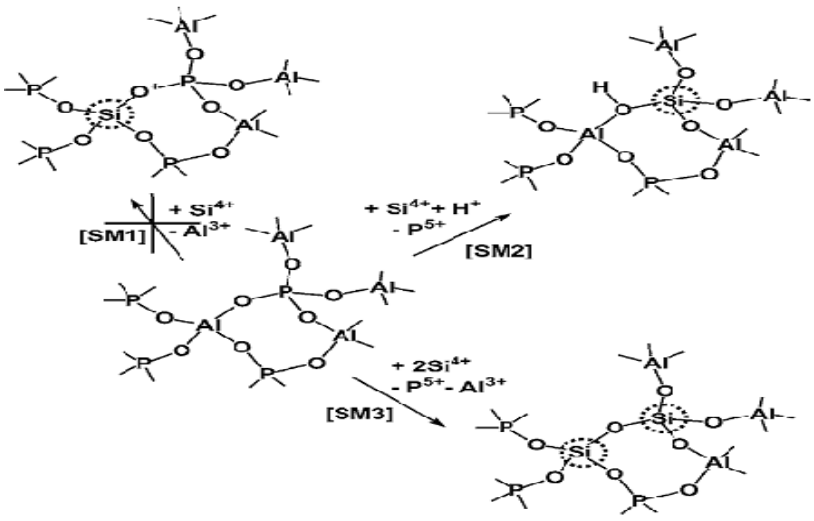
The pore blocking of mordenite can be reduced by dealumination without a loss in crystallinity to generating a mesopore system and for reducing the acid site density. Mild acid dealumination of H-MOR can often result in a more active catalyst due to the removal of an amorphous material from the zeolite channels and the generation of stronger acid site that can lead to both activity and selectivity improvements for particular reactions. Such effect was attributed to the presence of fewer and stronger Brønsted acid sites [32].

Mordenite has variety applications such as isomerization of n-butane [33], for the conversion of methanol to dimethyl ether [34], conversion of ethanol to ethylene [35]. Moreau et al. [29] reported the conversion of fructose to HMF over H-mordenites by

using water as reaction media and methyl isobutyl ketone (MIBK) as extracting solvent and obtained a higher selectivity of 92 % with a Si/Al ratio of 11. Considering these insights we want also to produce HMF starting from glucose which needs first to be isomerized to fructose because the formation of HMF was supposed to take place through the dehydration of a five membered monosaccharide ring. And hence in this study, the catalytic efficiency of mordenite in the conversion of Glucose to HMF will be examined.

1.3.2. Silicoaluminophosphates

Silicon-substituted aluminophosphate (AlPOs) molecular sieves are also interesting due to their controlled acidity that may be used as catalysts in various reactions. AlPO has a neutral framework and addition of silicon my replace either Al or P or both. Replacement of Al alone (SM1) is not possible as there is no possibility of cationic vacant frame work i.e. would lead the formation of Si-O-P bridges which are very unstable. If it replaces P alone (SM2), it will create anionic vacant site which will be compensated by a proton either from template or from acid. If it replaces both Al and P (SM3) a hydrophobic neutral frame work will form and responsible for the formation of extended silicon islands [36-39]. Combination of SM2 and SM3 also leads large Si islands and less number of acid sites but stronger than the acid sites formed by isolated Si atoms ($Si(OAl)_4$) i.e. SM2 mechanism. By doing so, the acidity of the materials can be controlled for selected reactions that we want to plan.



Scheme 6 Si substitution mechanisms in AlPO framework

During the synthesis of SAPOs different organic molecules (SDAs) can be used not only to direct the crystallization of the microporous structure but also influences the incorporation of Si into AlPO frame works. Accordingly, the SAPO-5 samples 1.5T and 1.5B reported by Gomez-Hortiguela et al. [36], have different Si distribution effect. The SAPO, 1.5T is synthesized by using triethylamine (TEA) as SDA, and have a higher water occlusion within the AFI structure which leads the material to be hydrophilic, while SAPO, 1.5B is synthesized by using benzylpyrollidine as SDA and have a lower water occlusion that leads the material to be hydrophobic. As a result, TEA molecules lead the incorporation of Si mainly as SM2 mechanism which have isolated Si atoms, $Si(OAl)_4$ and makes the material hydrophilic and that leads a number of Bronsted acid sites while BP molecules lead the incorporation of Si as mainly Si islands, $Si(OSi)_4$ and makes the material hydrophobic whose Bronsted acid site have a higher strength.

In our laboratory SAPO (1.5T) and 1.5B were tested for the conversion of glucose to HMF in IL [BMIM]Cl as solvent. But they were not effective for HMF production. This may be due to their low pore sizes than glucose or the active site may be blocked by the solvent [BMIM]Cl. And hence, in this study the catalytic activity of these catalysts will be examined for the conversion of glucose to a versatile platform chemical, HMF by using water/acetone as solvent.

In general a great advantage of using zeolites and zeotypes is that these catalysts, because of the specific structure of the pores and cages, not all products can be easily formed, and as a result can noticeably enhance the selectivity (i.e. the fraction of desired products of all products that are formed) of the reaction. In this study we used water as solvent because the use of ionic liquids is not compatible with zeolites due to their bulkier sizes that cannot diffuse out from the active site.

2. OBJECTIVE

2.1. General Objective

The main objective of this work is the production of 5-hydroxymethylfurfural from glucose by using SAPO-5 and Mordenite catalysts and water/acetone as a reaction media.

2.2. Specific objectives:

- To examine the catalytic performance of synthetic or modified mordenite, & SAPO-5 catalysts in water
- To characterize the produced 5-HMF by using NMR technique
- To quantify the product and the residue formed

3. EXPERIMENTAL PART

This part describes the materials and methods used in this work, procedure for the conversion of glucose to HMF and methods of analysis.

3.1. Chemicals and Apparatus

3.1.1. Chemicals

The materials and chemicals used in this study include: D-glucose anhydrous (dextrose) which is general purpose reagent (USA) BDH chemicals England, water, acetone (99.8%), ethyl acetate (99.5%), diethylether (99%), chloroform (99-99.4%), deuterated chloroform, deuterated water, NaCl, Mordenite was obtained from Zeolyst, and SAPO-5 catalysts were kindly donated by Dr. Luis Gomez-Hortigüela from the Institute of Catalysis and Petroleochemistry (ICP-CSIC)-Spain.

3.1.2. Apparatus and Instruments

Bruker 400 MHz spectrophotometer for the NMR analysis (both qualitative and quantitative aspect) of the extraction products and residues and a Perkin-Elmer TGA7 for the assessment of amount of organic molecules in the recovered catalysts were used.

3.2. Activation of catalysts

The commercial Mordenite from Zeolyst international CBV-21A (SiO_2/Al_2O_3= 20), in which ammonium ion is a nominal cation was calcined for six hours at 500 ^oC with a rate of 10°C/min to obtain the H-form. Similar procedure was used for the calcination of SAPO-5 materials (1.5T, and 1.5B) except the temperature was at 600 ^oC to remove water and organic molecules. Mordenite was also modified in our lab by using two modification procedures. In one method mordenite treated with 3M NH_4Ac and 2.4M NH_4F and the sample was labeled as WIM-1 (Si/Al =11.46). In the other method of modification, mordenite was dissolved in 3 M NH_4Cl and 2.4 M NH_4F and the sample was labeled as WIM-7 (Si/Al =12.5). The two samples show different textural properties than the parent Mordenite.

3.3. Catalytic experiments

The catalytic experiments were performed in a one necked 250mL round bottom flask under refluxing on an oil bath.

A. Monophasic system

In a typical reaction, 5g of D-glucose was added into a one necked 250mL round bottom flask and 35g/35 g of water/acetone (50/50% wt) was added with stirring until it was dissolved completely. Then 0.5 g of mordenite catalyst (CBV21A, WIM-1 and WIM-7), 10 % based on glucose, was added in to the reaction mixture and stirred without heating until it was completely dissolved. The reaction mixture was placed into an oil bath, which was preheated to 100 ^{o}C and set with a magnetic stirrer, water condenser and thermometer. 7 g of the reaction mixture was taken into 100 mL beaker at different time intervals (30 min, 1 h, 3 h, 6 h, 9 h, 24 h and 48 h). The samples taken at each specified time were extracted with 15 mL ethyl acetate two times and 15 mL diethyl ether once by stirring with glass stirrer. Ethyl acetate and diethyl ether were removed from the extract by using rotary evaporation under reduced pressure. The extracted product was washed with chloroform and transferred into labeled vials and kept in a refrigerator for analysis.

In a similar reaction conditions as described above the reaction was repeated with water in the absence of acetone.

Synthesis of 5-HMF from glucose in water/acetone as solvent was also conducted following the similar procedure as above (A) except that, the catalyst was SAPO-5 (1.5T and 1.5B) and the oil bath was pre-heated to 120 ^{o}C.

B. Biphasic system

I. In a typical experiment; (1) 5g of glucose was dissolved with a mixed 8 g of water and 8 g of acetone with stirring and 0.5 g of MOR-CBV21A was added, (2) 0.25 g NaCl (5 % of glucose) which was dissolved in 2 g of water and 20 g ethyl acetate were prepared in another flask. These two samples were mixed and placed into an oil bath preheated at 150 ^{o}C with constant stirring. Samples were taken at 1 h, 3 h and 6 h. Ethyl acetate was removed from the extract by using rotary evaporation under reduced pressure. The extracted product was washed with chloroform and transferred into labeled vials and kept in a refrigerator for analysis.

II. Similarly the above procedure (I) was repeated without the addition of NaCl.

After extraction of the products from the reaction, the residue was filtered with suction filtration by washing it with distilled water to separate the catalyst from the residue. The recovered catalyst was run on a Perkin-Elmer TGA7 instrument to know the amount of weight loss of water and organic molecules that were occluded in the pores of catalysts.

3.4. NMR analysis of glucose, 5-HMF and residue

3.4.1. NMR analysis of glucose

For the calculation of glucose conversion 0.01 g of glucose was dissolved in small amount of deuterated DMSO and run on BRUKER 400 MHz NMR spectrometer.

3.4.2. NMR analysis of 5-HMF and residue

The different time reaction products were dissolved in deuterated chloroform in the presence of mesitylene (1, 3, 5-trimethylbenzene) as internal standard and that of the corresponding residues were dissolved with deuterated water, and run for analysis of glucose conversion and 5-HMF yield.

3.5. HMF quantification and glucose conversion

The yield of HMF will be calculated from the spectra of the product at the specified time by considering the integral area of HMF and that of integral area of internal standard (mesitylene), while the glucose conversion will be obtained from the spectra of the residue by using the integral area of the residue and that of pure glucose by considering ^{1}H NMR spectra. The glucose conversion (mol %) and 5-HMF yield (mol %) will be calculated as shown below based on the amount of glucose loaded at each reaction.

$$\text{(I) Mole of 5-HMF} = \frac{\text{Integral area of 5-HMF}}{\text{Integral area of std}} \text{x} \frac{\text{Proton of std}}{\text{Proton of 5-HMF}} \text{x mol of std}$$

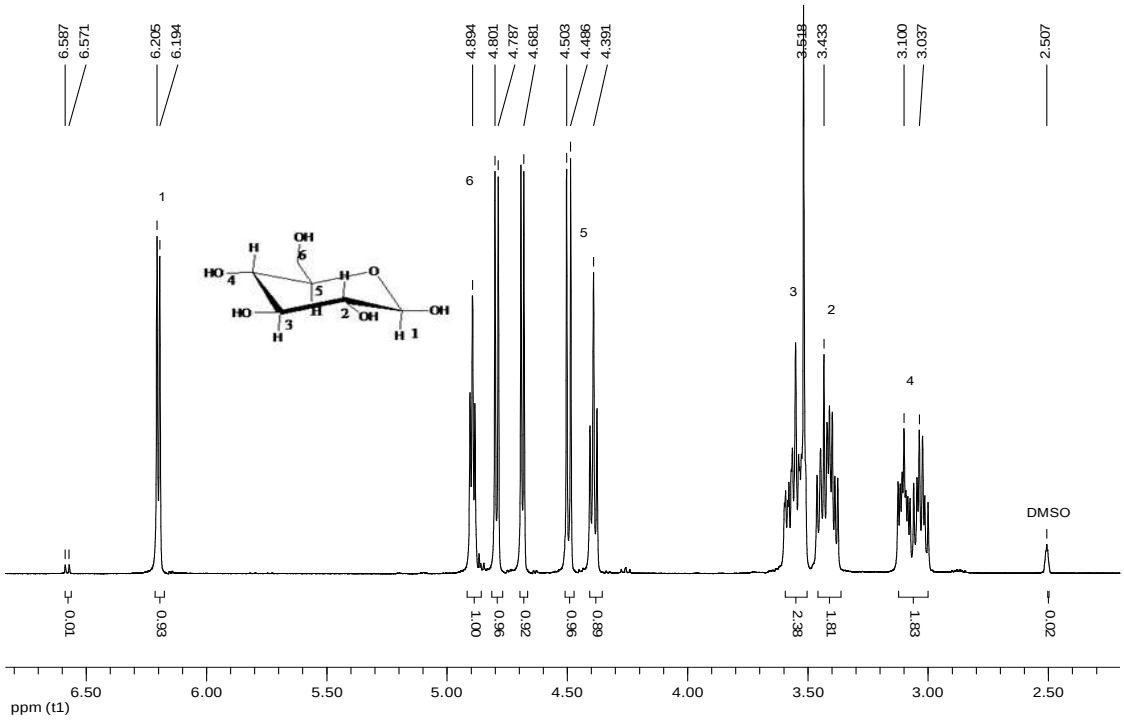
$$\text{(II) 5-HMF yield} = \frac{\text{Mole of 5-HMF obtained}}{\text{Mole of glucose loaded}} \text{x} 100\%$$

(III) $\%\ \text{Conversion} = (1 - \frac{\text{Mole of unreacted glucose}}{\text{Mole of loaded glucose}})\ \text{x}\,100\ \%$

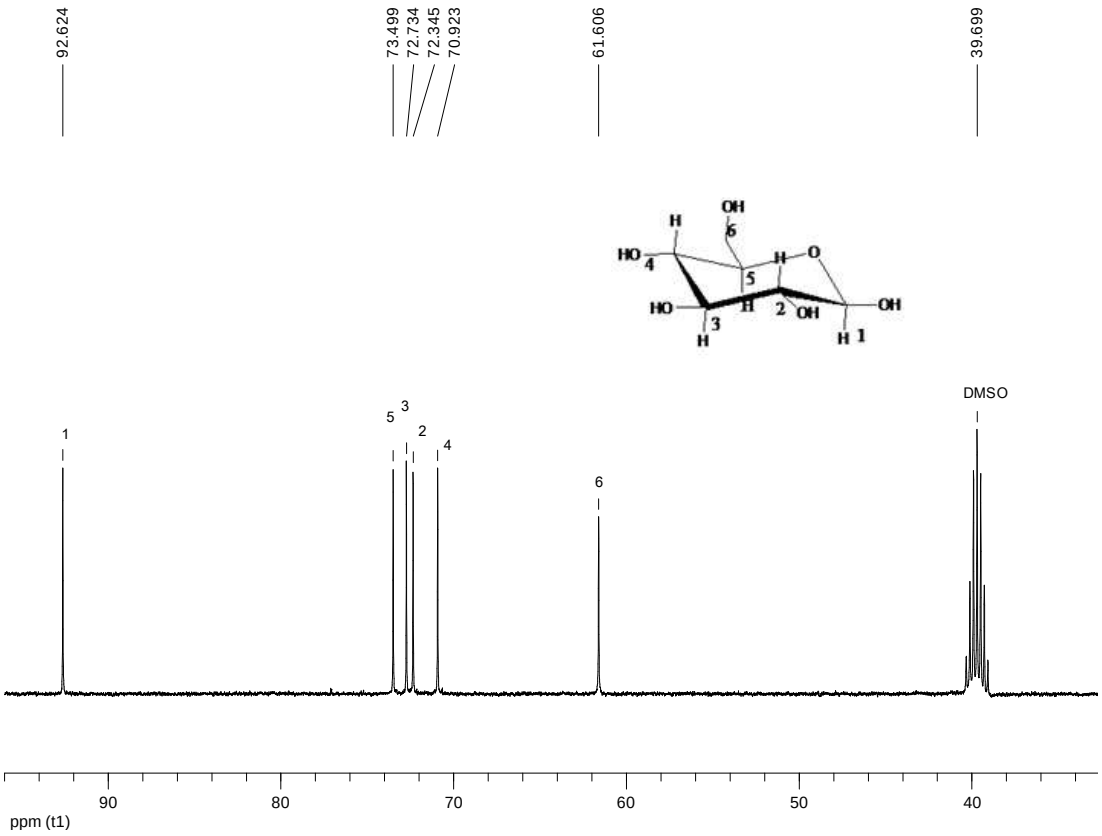
4. RESULTS AND DISCUSSION

4.1. NMR results of D-glucose

The ^{1}H and ^{13}C NMR of D-glucose are plotted in Figure 2. We take the integral areas of protons around a chemical shift of δ 3 in the pure glucose spectra and that of the residue to determine the amount of glucose converted.



(A)



(B)

Figure 2 (A) ^{1}H NMR and (B) ^{13}C NMR spectra of pure glucose, solvent DMSO

4.2. Catalytic conversion of glucose to 5-HMF by using Mordenite and SAPO-5 catalysts

In the catalytic conversion of glucose to HMF, different conditions including mono and biphasic systems were employed. The reaction temperature was varied from100 ^{o}C to150 ^{o}C and the ratio of catalyst to glucose 1:10 and that of glucose to water 1:7 were taken as the reaction condition. A summary of the reactions tried and the results are listed in Table 2.

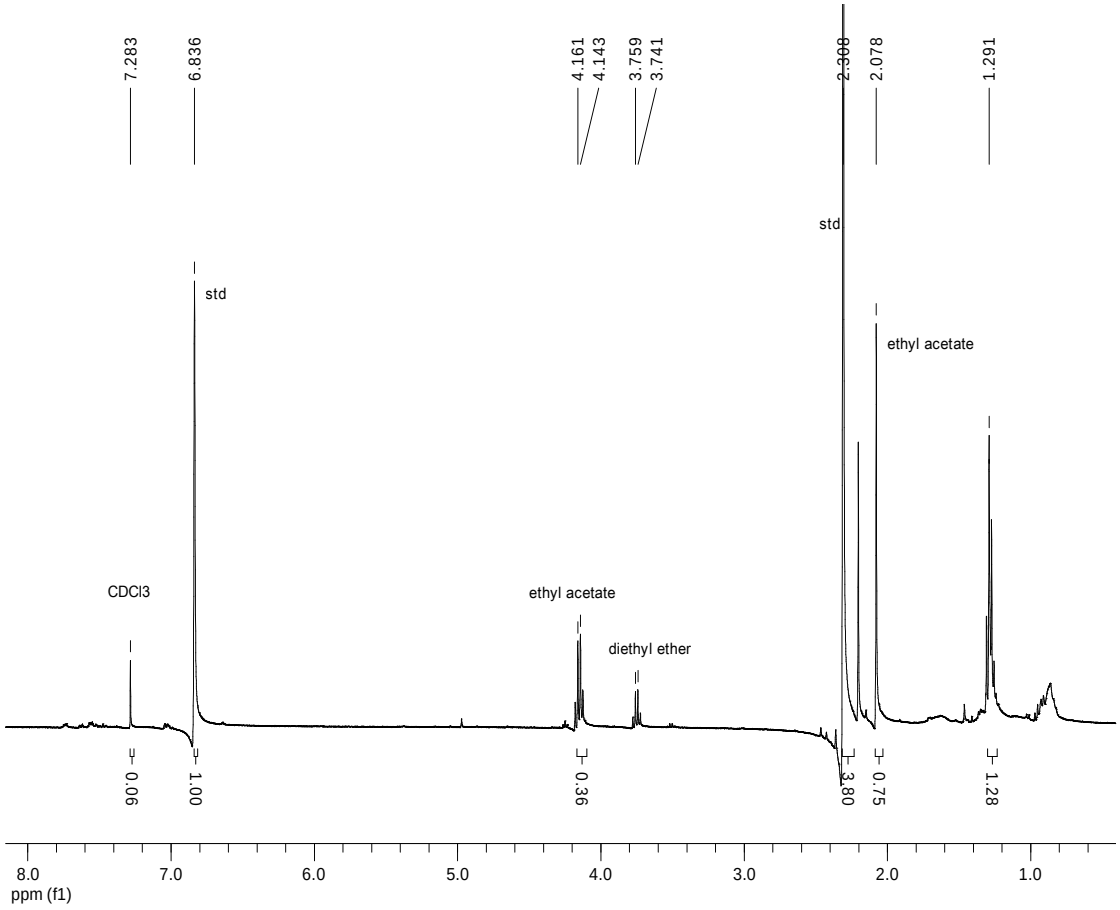
Table 1 Summary of the NMR results of the different reactions tried using Mordenite and SAPO-5 catalyst

Catalyst	Condition		Result
	Temp. ^{o}C	time	
CBV21A	100	30min	No product
CBV21A	100	6h	No product
CBV21A	100	24h	No product
CBV21A	100	48h	No product
WIM-7	100	30min	No product
WIM-7	100	6h	No product
WIM-7	100	24h	No product
WIM-7	100	48h	No product, residue shows presence of glucose
WIM-1	100	48h	No product
CBV-21A with NaCl	150	6h	Indicates only ^{1}H NMR of HMF
CBV-21A without NaCl	150	6h	Indicates only ^{1}H NMR of HMF
1.5T	120	24h	^{1}H, ^{13}C and DEPT shows signals of glucose
1.5B	120	24h	

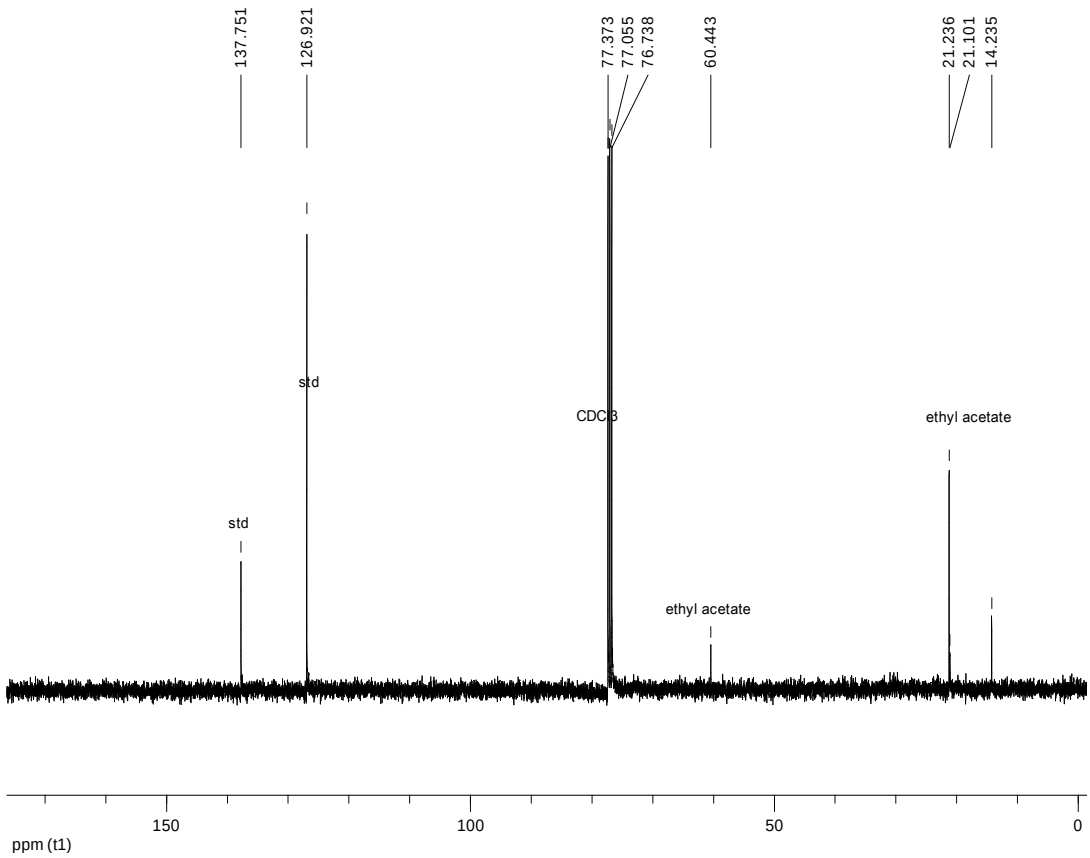
4.2.1. Catalytic conversion of glucose to 5-HMF using Mordenite at 100 ^{o}C

After the dehydration of glucose under the employed conditions, samples were taken at each specified time (30 min, 1h, 3 h, 6 h, 9 h, 24 h and 48 h) and extracted with ethyl acetate and diethyl ether followed by rotary evaporation under reduced pressure. After rotary evaporation of the different time products, some of them show slight yellow/ yellow color after the flask was washed with chloroform. But for reactions done with water after extraction and rotary evaporation no product was obtained after washing the flask with chloroform. And hence, we did not run the NMR of product as well as residue for reactions done with water only.

HMF was supposed to be the main reaction product; however, the NMR shows no signal for neither in ^{1}H nor in ^{13}C spectra other than extracting solvent. It also indicates that neither levulinic acid nor formic acid, which is the rehydration products of HMF, was detected. As noticed in table 3 the maximum glucose conversion is 28.41% and the spectra in Figure 3 indicates the absence of signals for HMF, as well as the byproducts (fig. 3 and appendices 2-9).



(A)



(B)

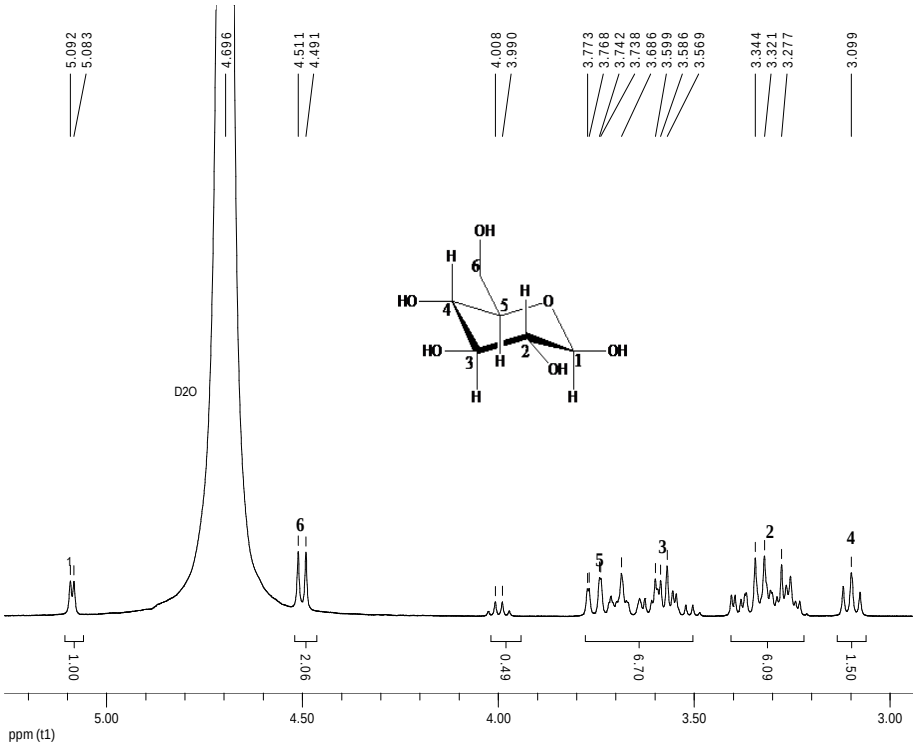
Figure 3 (A) ^{1}H NMR and (B) ^{13}C NMR spectra of 48 h reaction product of MOR-CBV21A catalyst at 100 ^{o}C

The NMR of the three residues analyzed tells us that there is glucose in the residue which indicates that the starting material was not properly converted to the desired product, 5-HMF as well as to other side products (fig. 4, appendices 10 -12). From table 3 below it is shown that the conversion of glucose by the three catalysts is very low, a maximum of 28.41 % in case of modified mordenite, WIM-7, at 100 ^{o}C and 48 h compared to SAPO-5 1.5T (13.66 % conversion) and 1.5B (18 % conversion) at 120 ^{o}C and 24 h. This conversion difference in mordenite (WIM-7) and SAPO-5 catalysts was due to the longer residence time of glucose in the reaction in the case of mordenite catalyst.

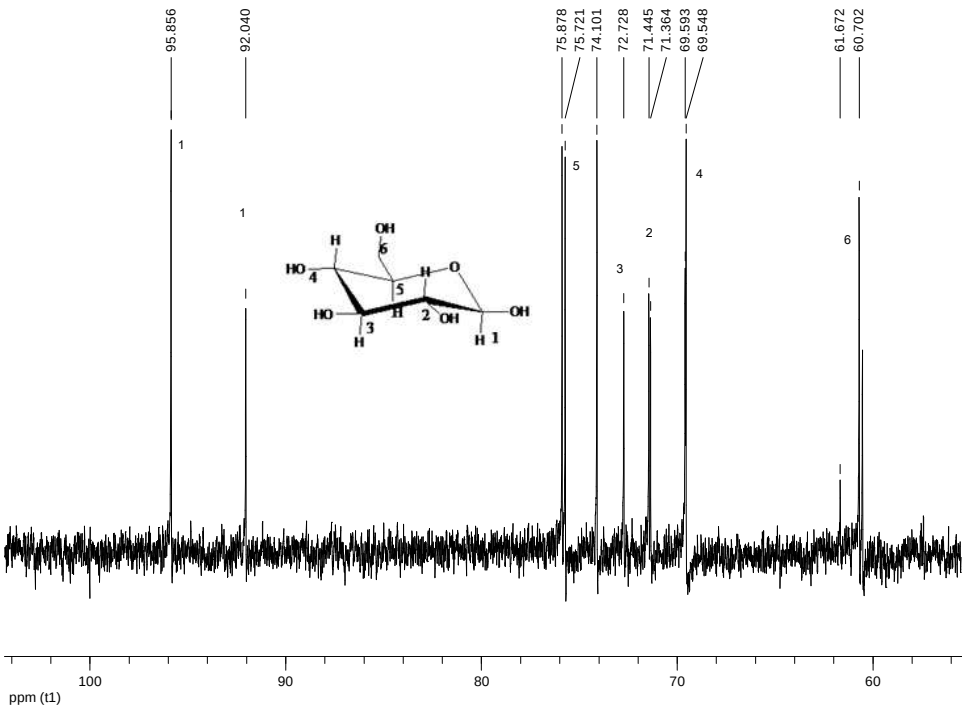
Table 2 quantitative results of conversion of glucose

Type of catalyst	Temp. ^{o}C	Time	Glucose conversion %
WIM-7	100	48h	28.41
1.5T	120	24h	13.66
1.5B	120	24h	18

For the SAPO-5 catalysts the difference in conversion may be due to their synthesis system by the inclusion of the structure directing agents. As reported by Gomez-Hortiguela et al [36] SAPO-5 synthesized with TEA as SDAs has a number of Bronsted acid sites and would interact each other and reduce the catalytic activity while SAPO-5 synthesized with BP which has a higher strength of Bronsted acid sites is more active and as result, responsible for the higher conversion.



(A)

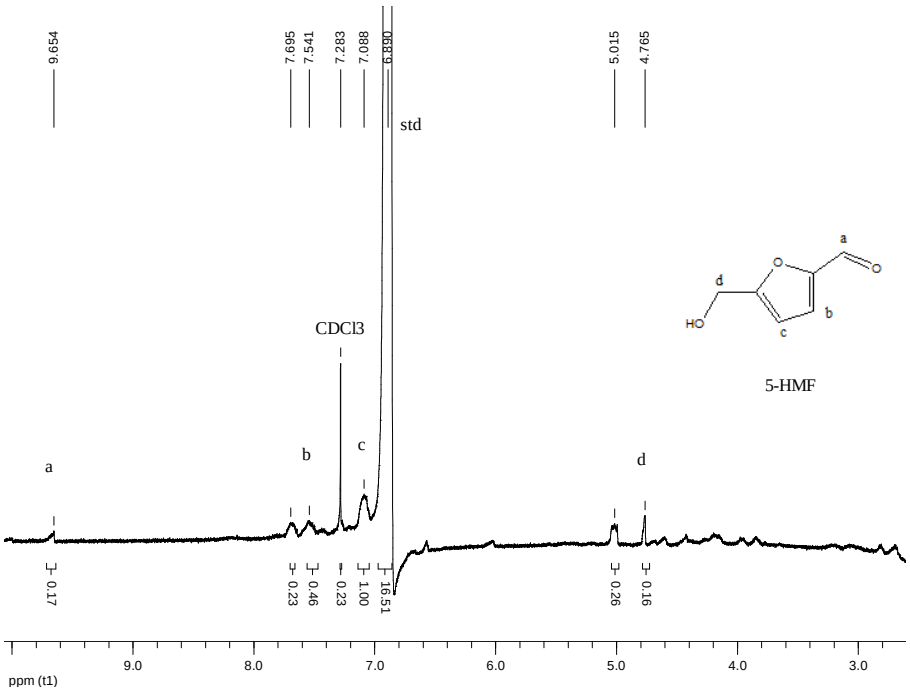


(B)

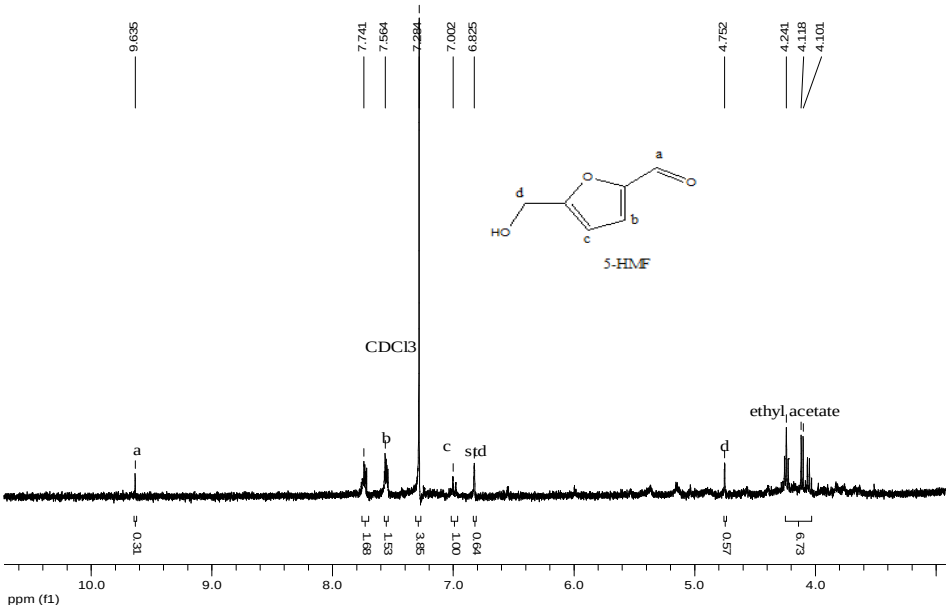
Figure 4 (A) ^{1}H and (B) ^{13}C NMR spectra of 24 h reaction residue of SAPO 1.5B catalyst at 120 ^{o}C

4.2.2. Catalytic conversion of glucose to 5-HMF using MOR-CBV-21A catalyst in biphasic system

In this part, we report the conversion of glucose to HMF in a biphasic system in the presence of MOR-CBV-21A at 150 ^{o}C. The biphasic reactor consists of an aqueous layer saturated with/without sodium chloride, glucose, and an extracting organic layer of ethyl acetate. The motivation for using a biphasic reactor is that the reactive HMF product can be continuously extracted from the aqueous phase by shortening the residence time of the intermediate, 5-HMF, thereby minimizing condensation reactions of HMF with glucose that lead to solid humins and rehydration reactions of HMF to form levulinic and formic acid. As noticed in the monophasic systems there are no sensible production of HMF or byproducts. And hence, we used biphasic system and the sample taken at 6 h gave yellow oil like product after rotary evaporation. The product was analyzed with NMR as shown in fig. 5 below and appendix 13.



(A)



(B)

Figure 5 ^{1}H NMR spectra of 6 h biphasic reaction product of MOR-CBV-21A catalyst at 150 ^{o}C (A) with NaCl and (B) without NaCl

The ^{1}H NMR spectrum (figure 5) above shows small peaks at δ 9.65 (s, 1H), δ 7.54 (d, 1H), δ7.08 (d, 1H) and at δ4.76 (s, 2H) for a reaction done with NaCl (A) as the partition and δ 9.63 (s, 1H), δ 7.56 (d, 1H), δ7.0 (d, 1H) and at δ4.75 (s, 2H) for a reaction done without NaCl (B) as the partition which are typical signals of HMF. It should be pointed out that no noticeable by-product signal was observed in the spectra and showed only HMF, the standards and unpurified ethyl acetate signals. The ^{13}C NMR spectra (appendix 13) showed no information about the presence of 5-HMF. The spectra showed only the standard and ethyl acetate signals. From table 4 it is noticed that the maximum yield of HMF is 7.38 % for a biphasic reactor system done without NaCl which is very low that indicates the concentration of HMF is very low. Hence, the absence of peaks of HMF in the ^{13}C NMR could be related with the very low concentration of HMF in the reaction product.

Table 3 HMF yields of MOR-CBV-21A catalyzed dehydration of glucose in water/acetone -ethyl acetate biphasic system at 150 ^{o}C

Catalyst	Yield %
MOR-CBV-21A with NaCl	1.2
MOR-CBV-21A without NaCl	7.38

Conditions: 8g/8g water/acetone, 5g glucose, 0.5g CBV-21A, 20g ethyl acetate, 150 ^{o}C, 6h.

From table 3 above it is observed that the maximum HMF yield is 7.38% which was done in the absence of NaCl as the partition. It was supposed that the application of NaCl was used to increase the selectivity of HMF and to push it to the organic extracting phase by salting out effect [21]. In our study the catalyst that we used was H-mordenite and zeolites by their nature have ion-exchange properties, and hence the addition of NaCl salt to the solution may create cation exchange between Na^{+} of the salt and H^{+} of the mordenite resulting Na-MOR, which may suppress the catalytic property of H-MOR. As the result, the conversion of glucose to HMF may be reduced. And hence, this effect contributes to the low yield of HMF when the conversion was done in the presence of NaCl as the partition (yield 1.2%) compared to the one done without NaCl (yield 7.38%).

4.2.3. Thermogravimetric analysis of the recovered catalysts

The catalytic activity and diffusion problem of catalysts can be assessed by using thermal gravimetric analysis that tells materials stability as a function of temperature. The TGA plot of all the catalysts show one weight loss below 100 ^{o}C that is assigned to the removal of water on the external surface of the catalyst (hydroscopic water). Some of the catalysts also show sharp weight losses in the range between 100 to 200 ^{o}C indicating desorption of water loosely bound to the catalysts. Temperatures above 200 ^{o}C showed several weight loss steps which extends to above 700 ^{o}C, evidencing to desorption of undiffused organic molecules or the glucose stacked in the pores of the catalysts.

Table 4 TGA results of the recovered mordenite and SAPO-5 catalysts

Recovered catalyst	Reaction temperature	Weight loss (%)			
		<100 ^{o}C	100-200 ^{o}C	>200 ^{o}C	Total weight loss (%)
CBV21A	100 ^{o}C	2.8	5.2	31.57	39.57
WIM-7	100 ^{o}C	4	-	14.22	18.22
WIM-1	100 ^{o}C	2.24	5.57	39.74	47.55
SAPO 1.5T	120 ^{o}C	8.61	-	11.56	20.17
SAPO 1.5B	120 ^{o}C	4.17	6.57	14.44	25.18
CBV21A,	150 ^{o}C	3.27	-	19.73	23
CBV21A with NaCl & biphasic	150 ^{o}C	1.72	-	40.42	42.14
CBV21A without NaCl & biphasic	150 ^{o}C	4.02	-	11.88	15.9

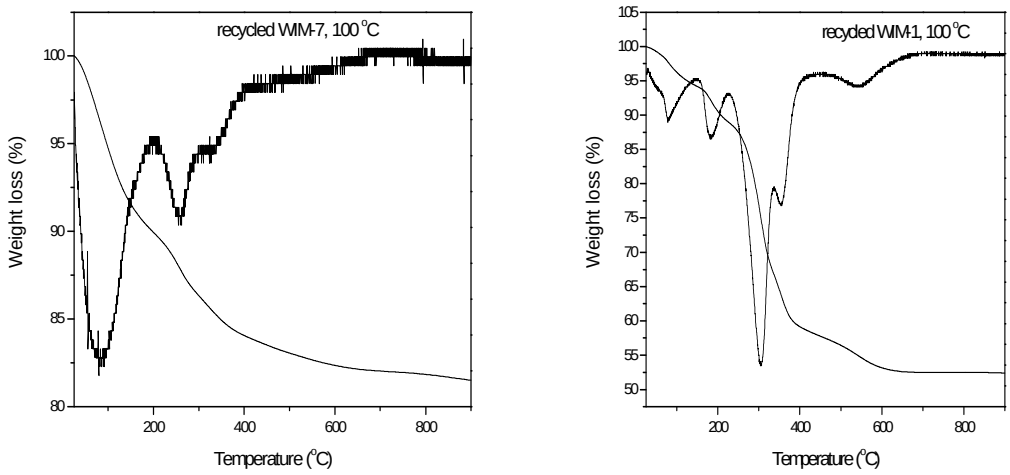


Figure 6 TGA plot of the recovered modified mordenite catalysts

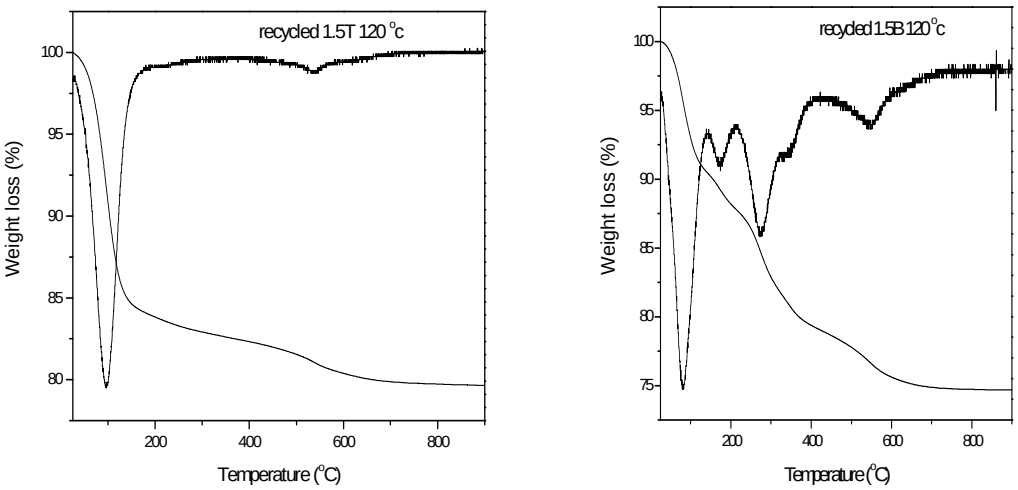


Figure 7 the TGA of the recovered SAPO-5 catalysts

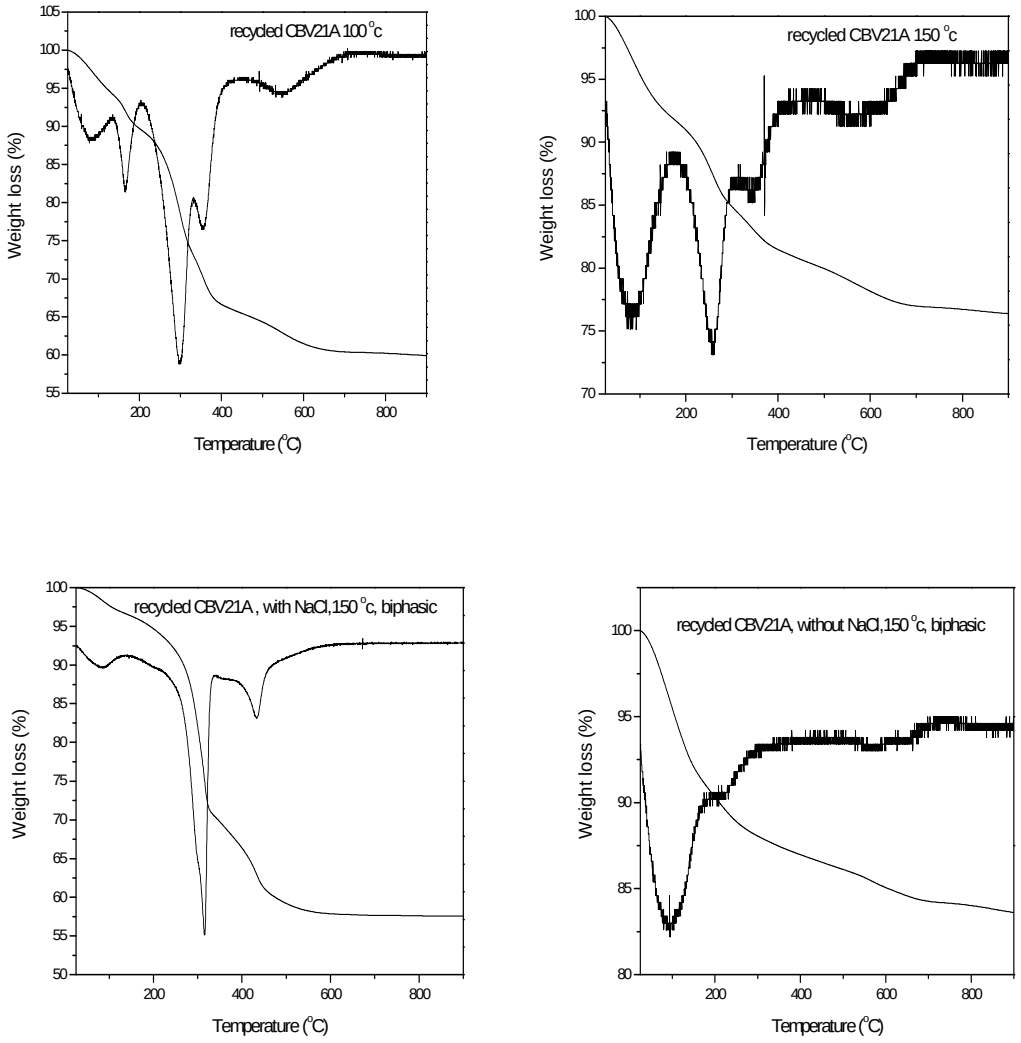


Figure 8 TGA plots of the recovered CBV21A catalyst

4.3. Effects of Reaction conditions on the glucose dehydration to HMF

4.3.1. Effect of reaction time

Varying the reaction time showed no differences in the dehydration of D-glucose catalyzed by Mordenite and SAPO-5 as shown in NMR results. The spectra indicate only the signal of extracting solvents. As a result we could not quantify the HMF yield, even if we could calculate the conversion. The glucose conversion (28.41%) at 48h for WIM-7, 13.66% for 1.5T and 18% for 1.5B at 24h indicates that glucose could not converted well

by extending the reaction time longer. These conversion values confirm that glucose was converted to humins and isomerized products. The TGA graphs also showed the presence of diffusion problem. So, this problem also supports the NMR spectra of the different time reaction products that do not show reasonable signal for HMF as well as for byproducts. And hence, varying the reaction time has no more difference for production of HMF in our study.

4.3.2. Effect of catalysts on the reaction

The glucose conversion would be affected by the type of catalyst used during the reaction. The catalysts used were mordenite, which has a pore diameter of 7Å and SAPO-5 has a pore diameter of 7.3 Å that of our sugar glucose has 8.6 Å. Pore widths of at least 10 Å allowed the 8.6 Å glucose molecules to diffuse and react directly within the micro- and mesopores of the catalyst. The principal reactions occurring in this manner being: the isomerization of glucose to fructose, dehydration of glucose to 5-HMF, rehydration of HMF to formic acid and levulinic acid. The conversion of glucose, a maximum of 28% with modified mordenite WIM-7, showed that glucose is not well converted with the catalyst which has less pore diameter than glucose. Glucose may not be purely cyclic [40, 41], and it may contain some fraction of open chain components in solution. The acyclic form of glucose may come in to the pore of the catalysts due to its some structural linearity. Such a part of glucose might be converted to HMF, but due to its large pore size (9.3 Å) than the catalyst it could not diffused out from the pore of the catalysts. It may also rehydrate to acids, but they will isomerized to other products that could not diffused out. The NMR spectra of products done with the monophasic reactor system (appendices 2-9) showed no signal either for HMF or the rehydration products levulinic or formic acid. The spectrum only shows the signal of the solvents used for extraction. This idea could be supported by the spectra of residues run for modified mordenite WIM-7, SAPO 1.5T and 1.5B. These spectra (fig 4, appendices 10-12) also indicate the signal of unreacted glucose. The TGA plot of the catalysts also prevail the presence of diffusion problem. For example, the TGA of WIM-7 fig. 6 showed a total weight loss of 18.22%, from this 4% weight lost below 100 ^{o}C that could assigned due to the desorption of water that might be adsorbed on the external surface of the catalyst during reaction and filtration. The remaining 14.22% assigned to desorption of undiffused organic molecules

which may be HMF, isomerized products or some part of glucose stacked in the pores of the catalysts.

The catalytic activity is also influenced by the acid strength of the catalyst sites which is determined by the Si/Al ratio. According to Moreau et al. [29] the aim is to increase activity, but a relatively low acidity is required for the dehydration step to 5-HMF. The selectivity tends to decrease by increasing the Si/Al ratio, i.e. by increasing the acidic properties of the catalysts, thus allowing secondary reactions to take place, such as the formation of formic and levulinic acid or polymeric materials referred to as humins. Consequently the catalyst mordenite CBV21A which have SiO_2/Al_2O_3 ratio = 20 is more acidic and is responsible for secondary reactions to take place, and that of WIM-7 (Si/Al ratio =12.5) even though the conversion is very low, 28.41% at 48h and 100 ^oC. At this amount of conversion 5-HMF would be formed and it might rehydrate to levulinic acid or formic acid by the solvent water even its concentration is very low. The spectra of the products (appendices 2-9 and fig. 3) confirms that there is no signal either for 5-HMF or for the byproducts in the monophasic systems due to the very low concentration of the products. The TGA graphs of recovered catalysts also evidenced that some molecules are stacked in the catalysts.

Structure directing agents used during the synthesis of the catalyst could also influence catalytic activity of the catalyst. The SAPO-5 materials 1.5T and 1.5B are synthesized in different SDAs which have different ability to convert glucose: 13.66% for 1.5T and 18% for 1.5B. The low conversion in case of 1.5T, in addition to its more acidic sites, is due to its hydrophilicity that absorbs more water. For 1.5B more organic molecules could occlude due to its hydrophobicity. The TGA of the recovered 1.5T showed 8.61 % weight loss while 1.5B showed 4.17 % below 100 ^oC assigned to desorption of water. From the TGA of SAPO 1.5T 0.58g of organic was occluded while 0.68g of converted glucose from NMR was obtained. Similarly for SAPO 1.5B 0.72g organic from TGA and 0.9g converted glucose and for WIM-7 0.71g organic from TGA and 1.42g converted glucose was obtained from NMR spectrums. Therefore, the conversion of glucose would be influenced by form of the catalyst used and the glucose converted and the amount of organic occluded was slightly comparable.

4.3.3. Effect of solvent

The dehydration reactions of glucose with mordenite and SAPO-5 catalysts were carried out in water/acetone as solvent in monophasic system and water/acetone-ethyl acetate in the biphasic systems refluxing under oil bath. In the case of monophasic system there was no noticeable signals for HMF as well as byproducts. The maximum 28.41% conversion of glucose also shows that the solvent water only dissolved glucose and had not catalytic application on the reaction system. Instead of that as reported by Kim et al. [42] there could be a strong interaction between the polar solvent (water) and the hydrophilic surface of the catalysts and water can block and/or poison the surface acidic sites.

On the other hand, even if the HMF yield is low in water/acetone-ethyl acetate biphasic system, it is better than the water/acetone monophasic system due to the driving force of the biphasic mixture in which HMF collects in the organic phase after its formation in the aqueous phase. This method of HMF synthesis in a biphasic solvent also produced 5-HMF as indicated from the ^{1}H NMR spectrums (fig. 5) of the HMF product collected from the ethyl acetate layer even if the signals are very weak. Even though water is a very green solvent compared to other solvents, it has disadvantages in the practical production of HMF from glucose, due to the rehydration of HMF and the formation of levulinic and formic acids as side-products.

5. CONCLUSION

The conversion of glucose to the platform chemical intermediate, 5-HMF was examined in different conditions including monophasic and biphasic reactor systems by using Bronsted acid catalysts mordenite and silicoaluminophosphate materials. The high conversion of glucose (28.41%) by using modified mordenite, WIM-7 as novel catalyst at 100 ^{o}C and 48 h indicates that the catalytic activity of the catalyst was suppressed by its channel dimension which have smaller pore dimension than the starting material glucose. The conversion is also very low to SAPO-5 catalysts; 13.66% conversion for 1.5T and 18% conversion with 1.5B at 120 ^{o}C and 24 h. As a result, glucose which has 8.6 Å pore diameter needed at least 10 Å pore dimension in order to diffuse out and react directly to the active site of the catalyst. Glucose may contain small amount of open chain in solution that may enter in to the reactive site of the catalyst. This acyclic glucose could be converted to HMF. But the TGA of the recovered catalysts illustrates that some organic molecules are occluded in the channels of the catalysts. This idea also supported from the NMR spectrums of the residue which showed a clear presence of glucose and the absence of signals for HMF or other byproducts from NMR spectra of different hour reaction products. This low conversion is also not only due to the catalytic efficiency but also due to the solvent effect. The solubility of glucose in water is very good but it has no any other effect as non-aqueous solvents and ionic liquids which have a slight catalytic effect on the conversion of hexoses. Instead it will interact with the surface of the catalyst and will inhibit catalytic activity of catalysts. As a result, mainly the shape selectivity of the pore size of zeolites and zeotypes contributes for the low conversion of glucose to HMF and/or to other side products.

In this work we also showed that HMF can be produced in biphasic reactor systems using ethyl acetate as the organic extracting phase in the presence as well as in the absence of NaCl as the partition agent and by using a Bronsted acidic catalyst MOR-CBV21A. But the yield difference results from the ion exchange of Na^{+} of the salt and H^{+} of the H-MOR resulting Na-MOR which has a very weak catalytic activity for the one done in the presence of NaCl. Thus, in this work biphasic systems gave a reasonable yield than the monophasic systems in water, even if the yields are very low.

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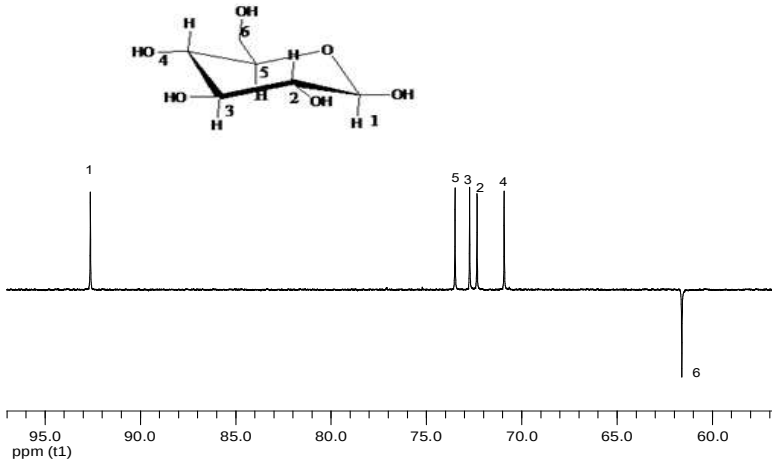
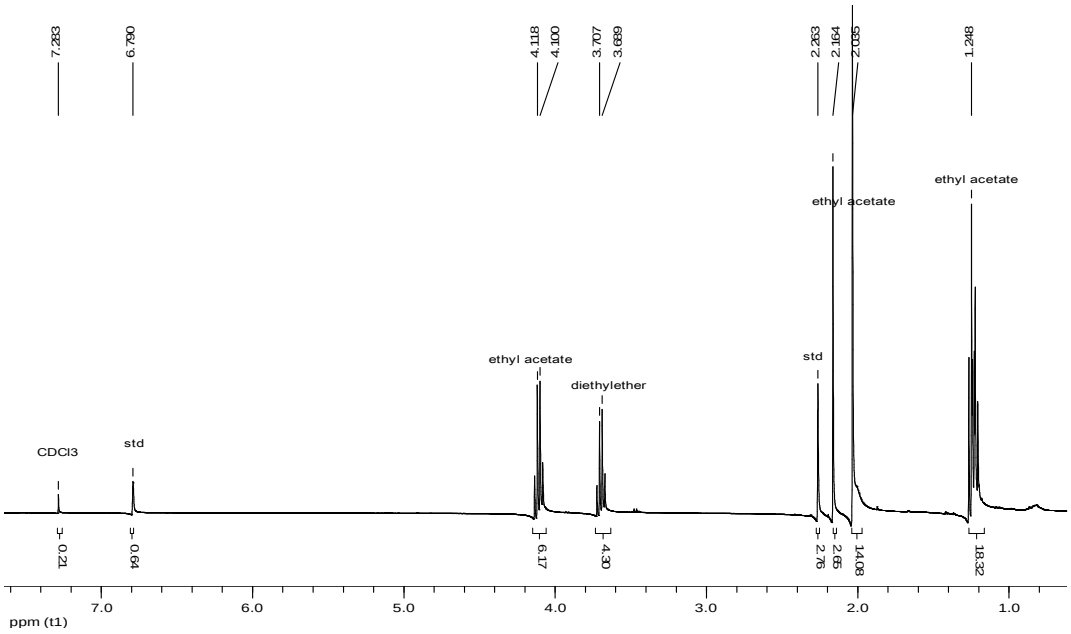
APPENDICES

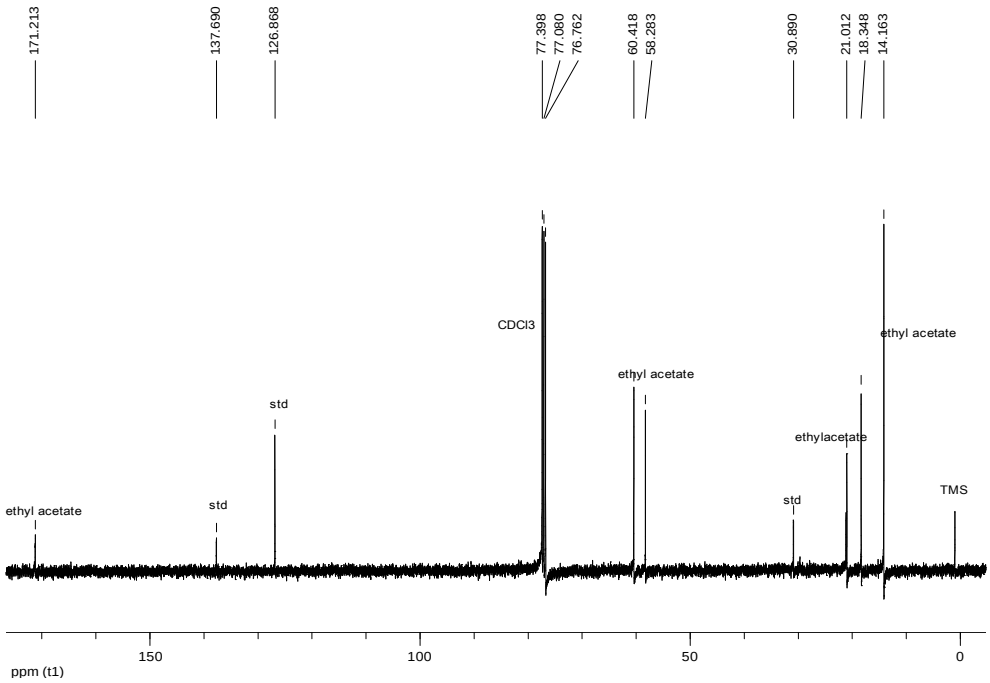
Appendix 1: DEPT spectra of pure glucose



Appendix 2: (A) ^{1}H and (B) ^{13}C NMR spectra of 30min reaction product of MOR-CBV-21A catalyst at 100 ^{o}C

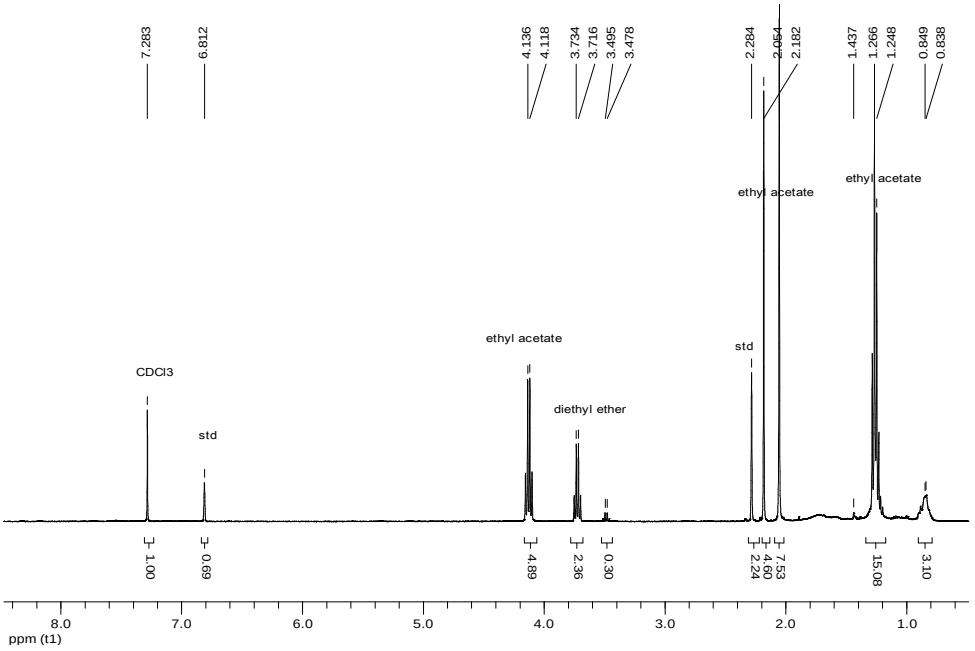


(A)

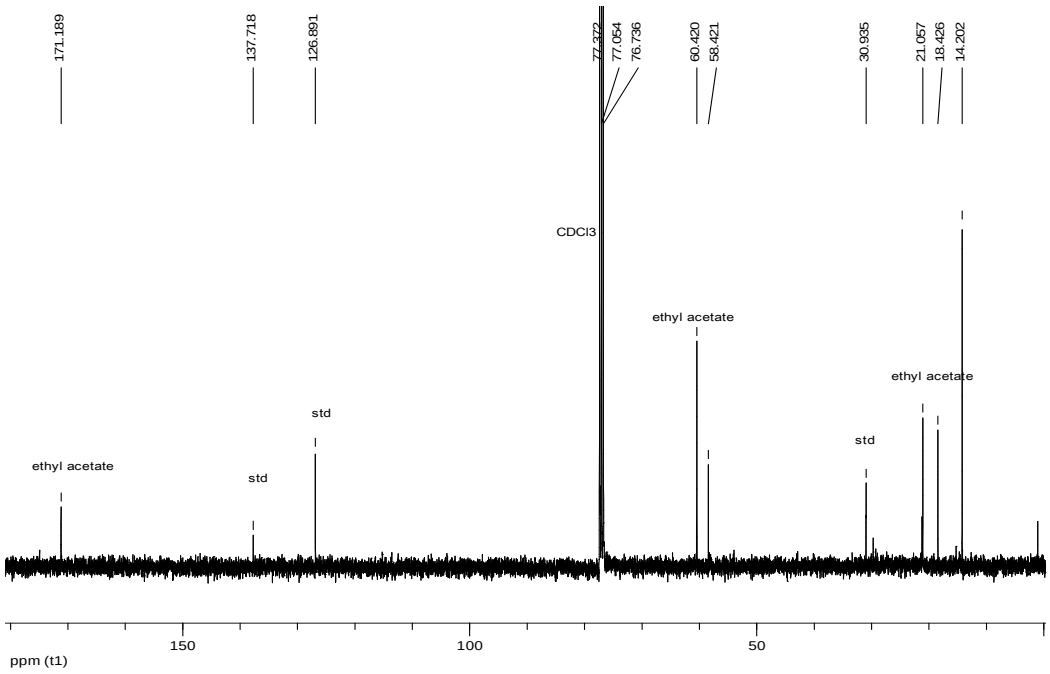


(B)

Appendix 3: (A) ^{1}H and (B) ^{13}C NMR spectra of 6h reaction product of MOR-CBV-21A catalyst at 100 ^{o}C

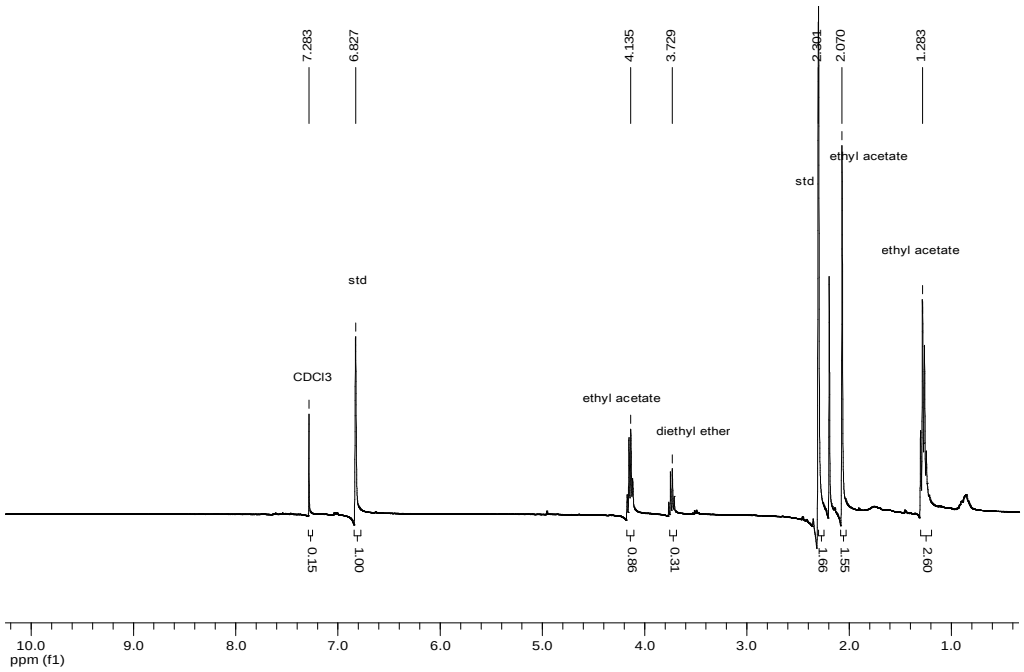


(A)

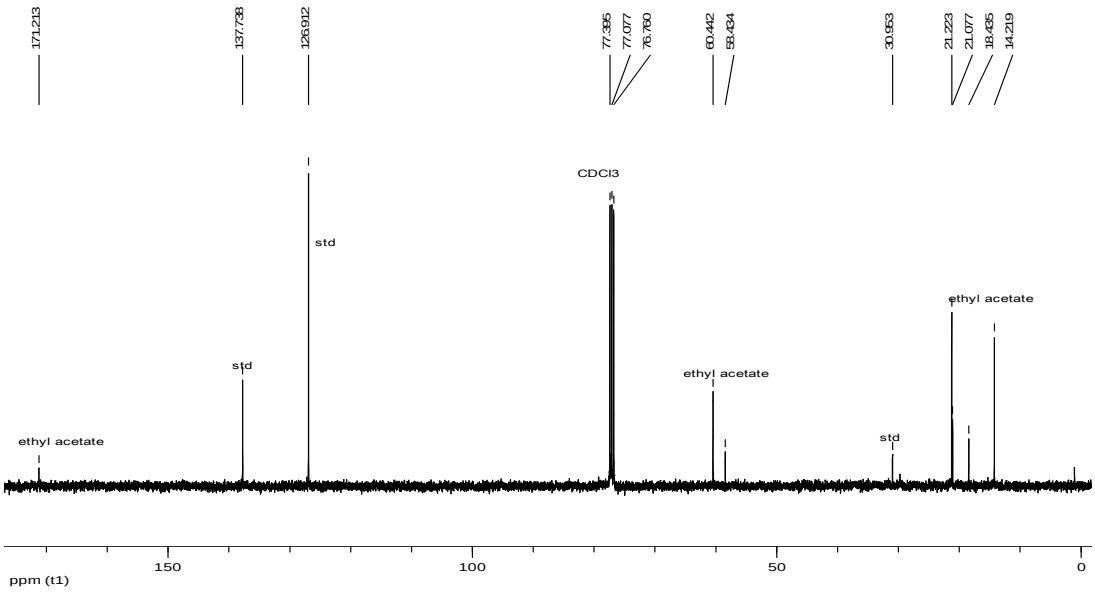


(B)

Appendix 4: (A) ^{1}H, (B) ^{13}C NMR spectra of 24h reaction product of MOR-CBV-21A catalyst at 100 ^{o}C

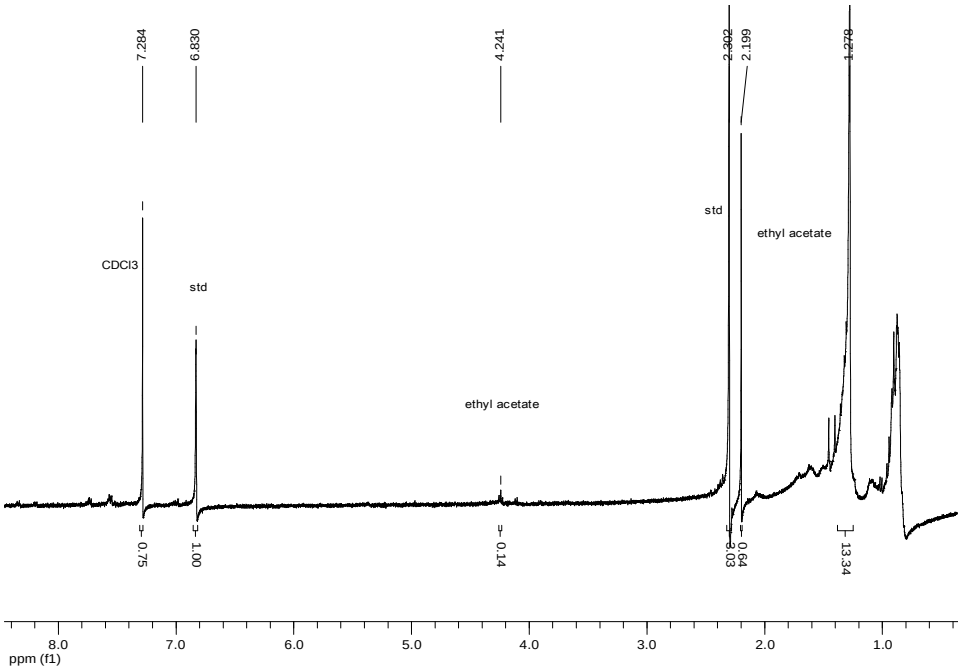


(A)

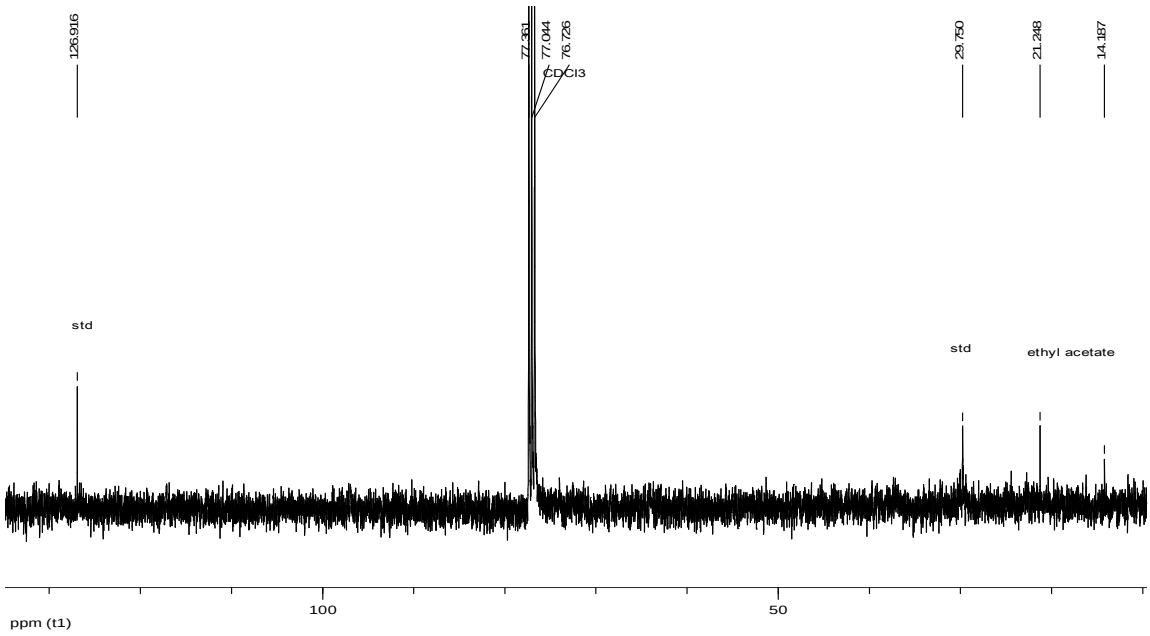


(B)

Appendix 5: (A) ^{1}H and (B) ^{13}C NMR spectra of 30min reaction product of WIM-7 catalyst at 100 ^{o}C

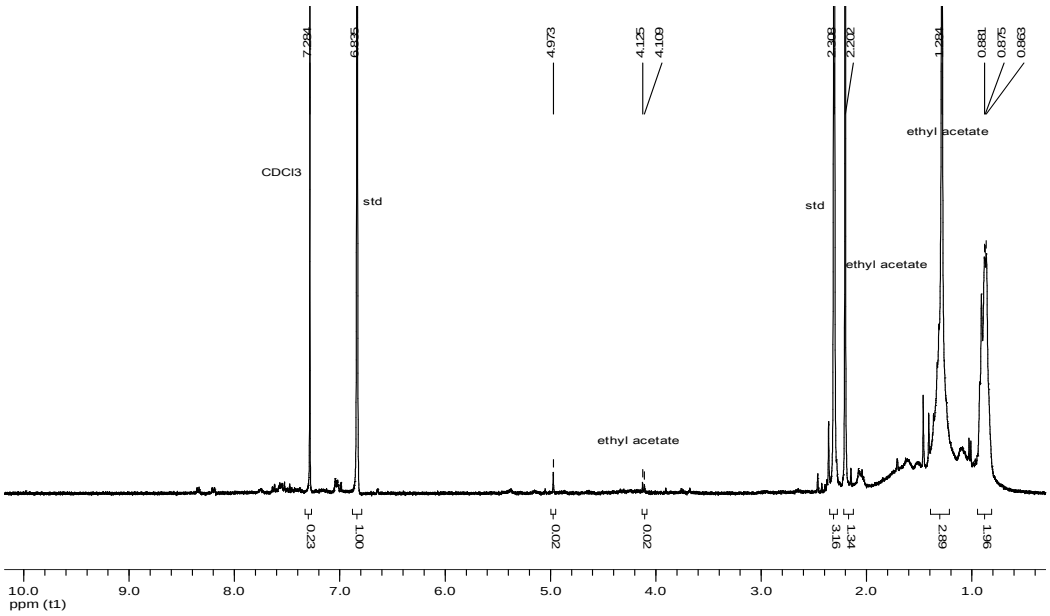


(A)

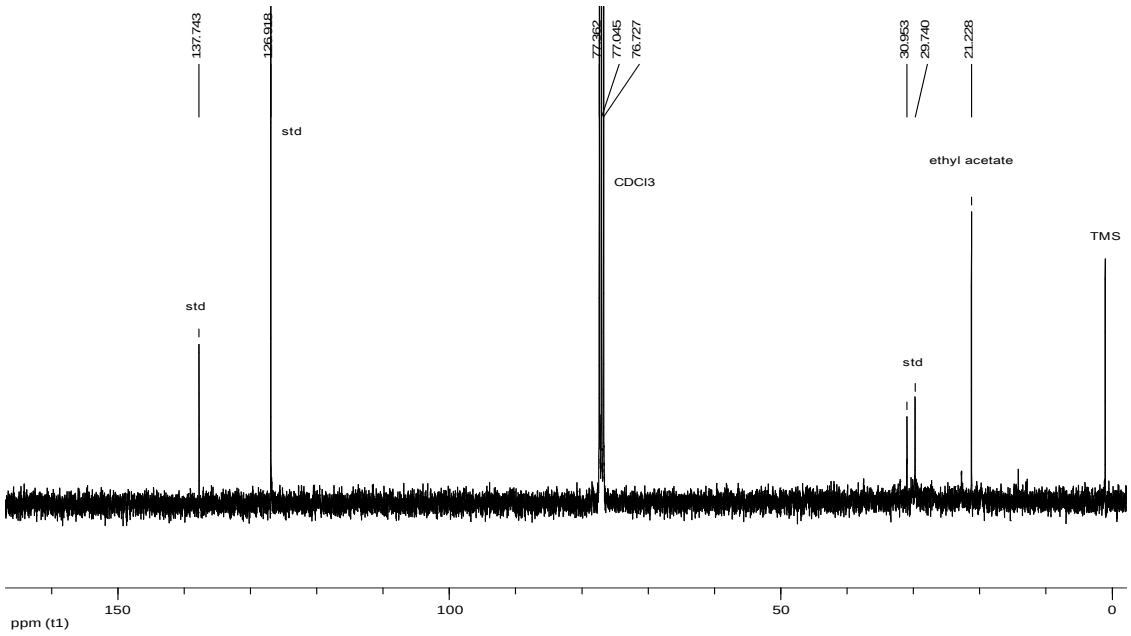


(B)

Appendix 6: (A) ^{1}H and (B) ^{13}C NMR spectra of 6h reaction product of WIM-7 catalyst at 100 ^{o}C

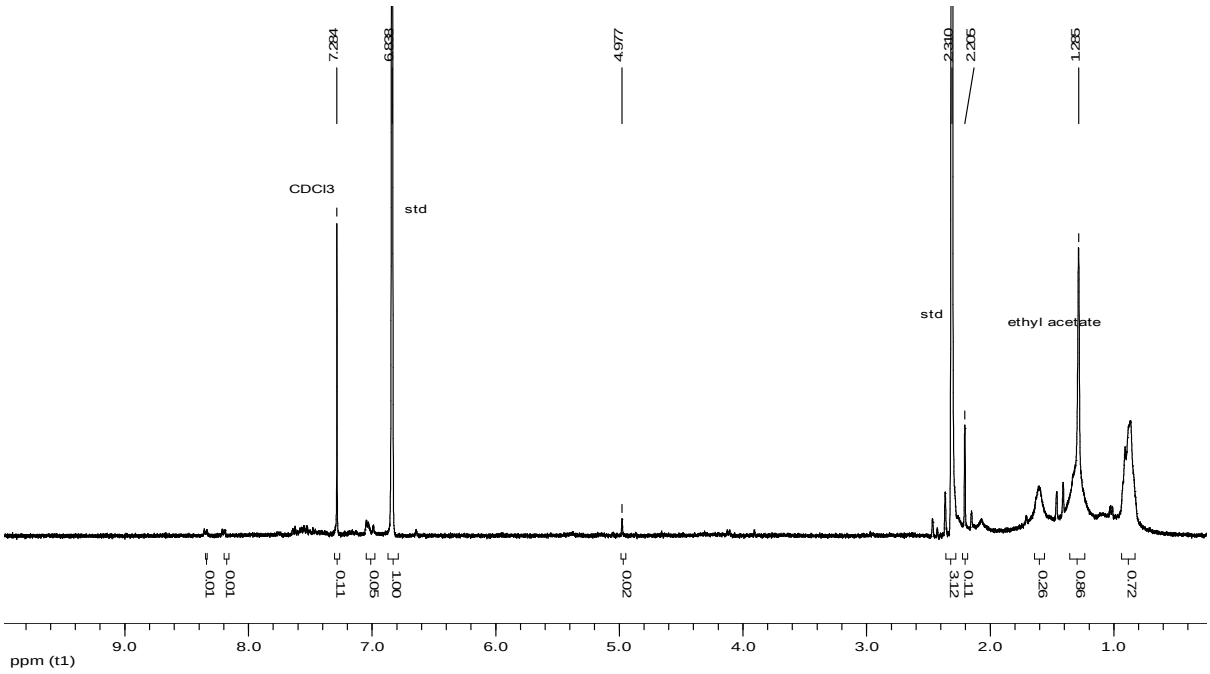


(A)

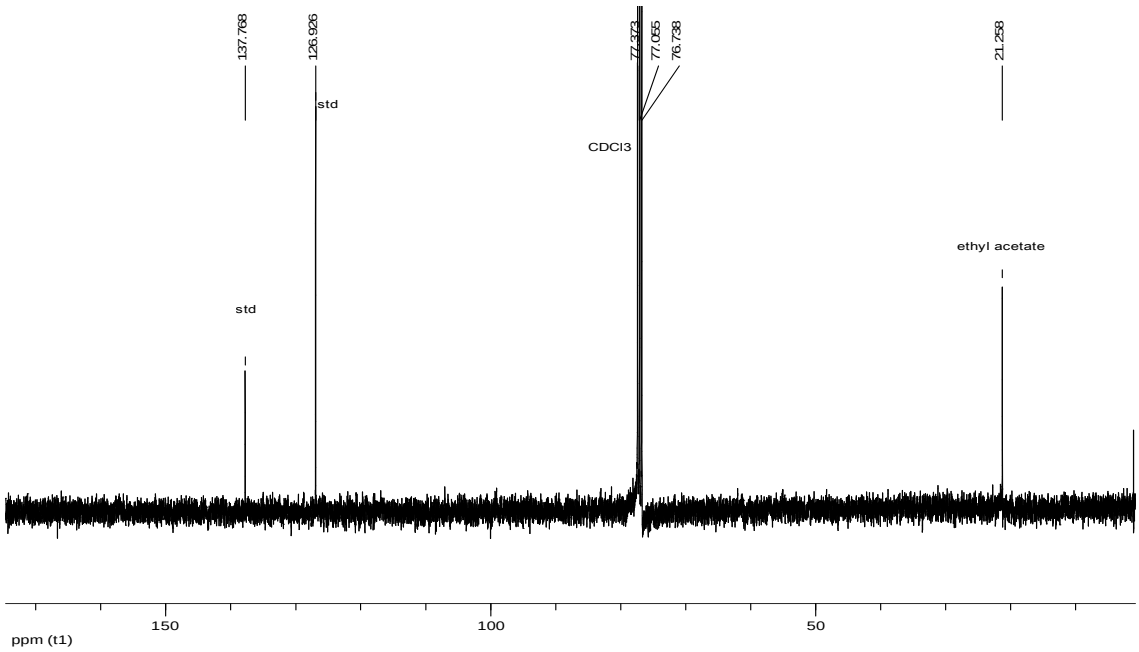


(B)

Appendix 7: (A) ^{1}H and (B) ^{13}C NMR spectra of 24h reaction product of WIM-7 catalyst at 100 ^{o}C

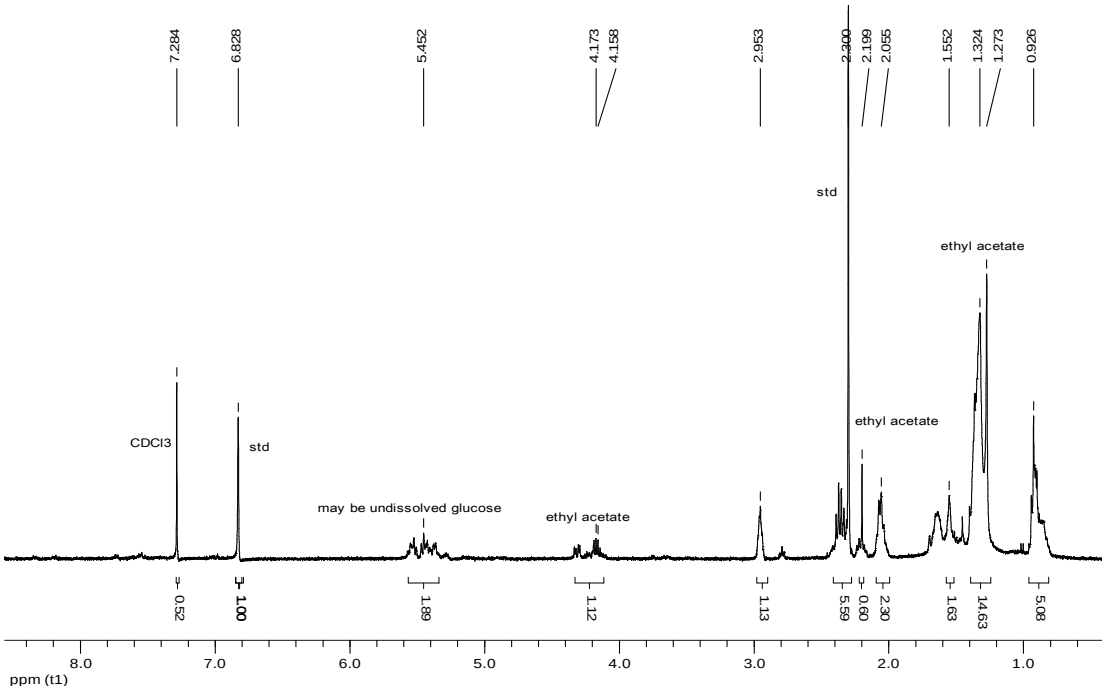


(A)

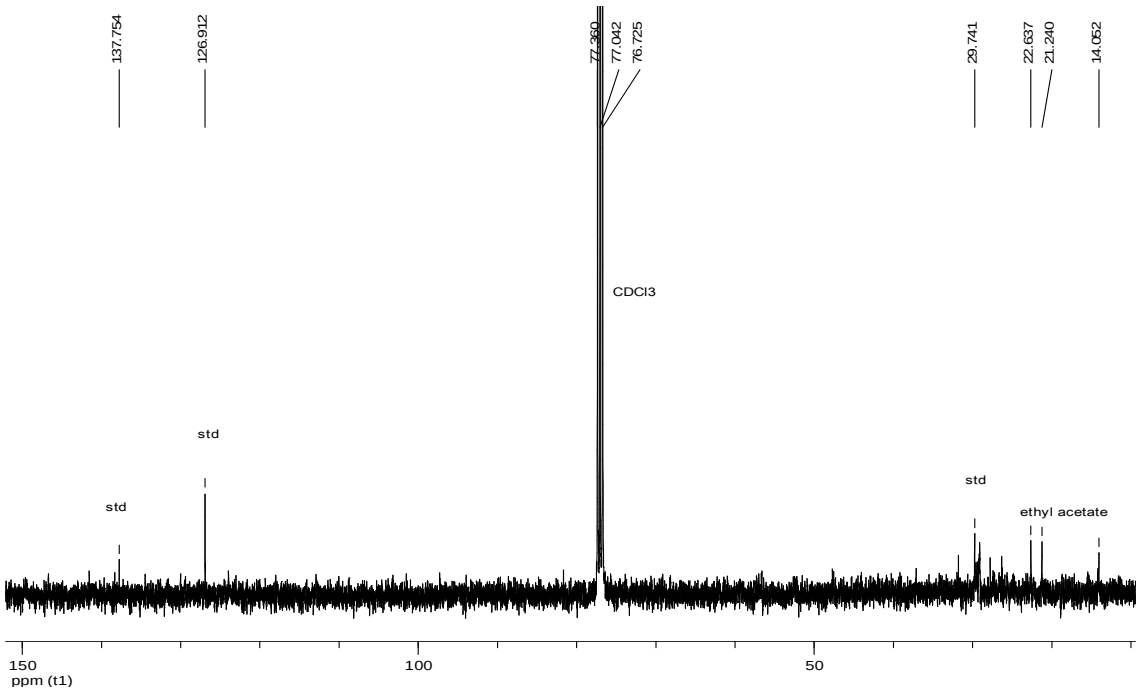


(B)

Appendix 8: (A) ^{1}H and (B) ^{13}C NMR spectra of 48h reaction product of WIM-7 catalyst at 100 ^{o}C

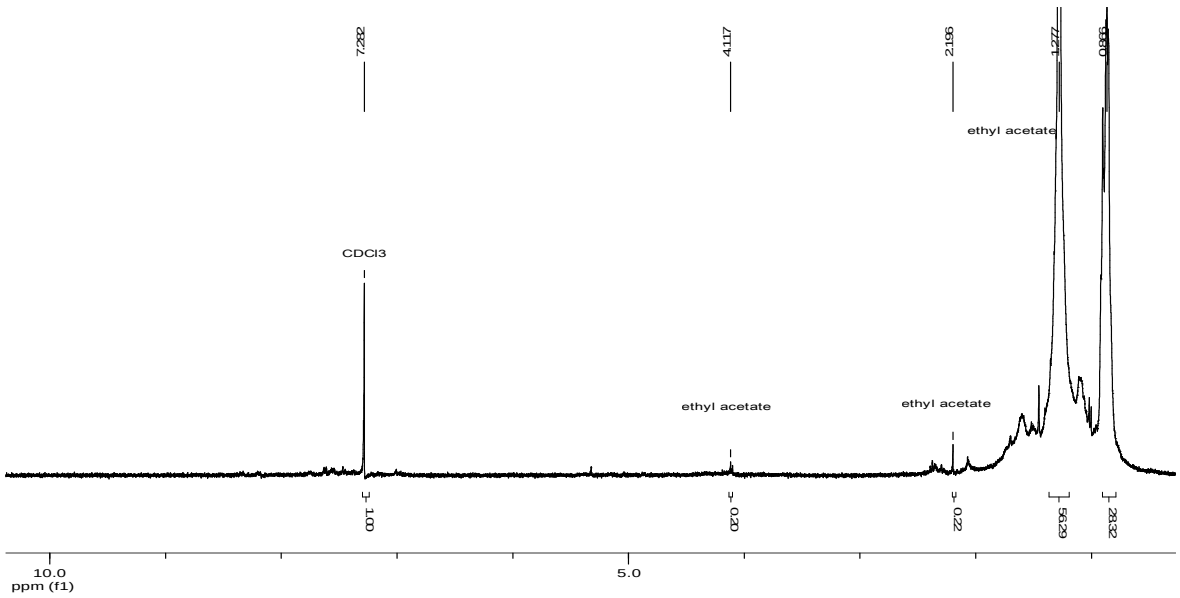


(A)

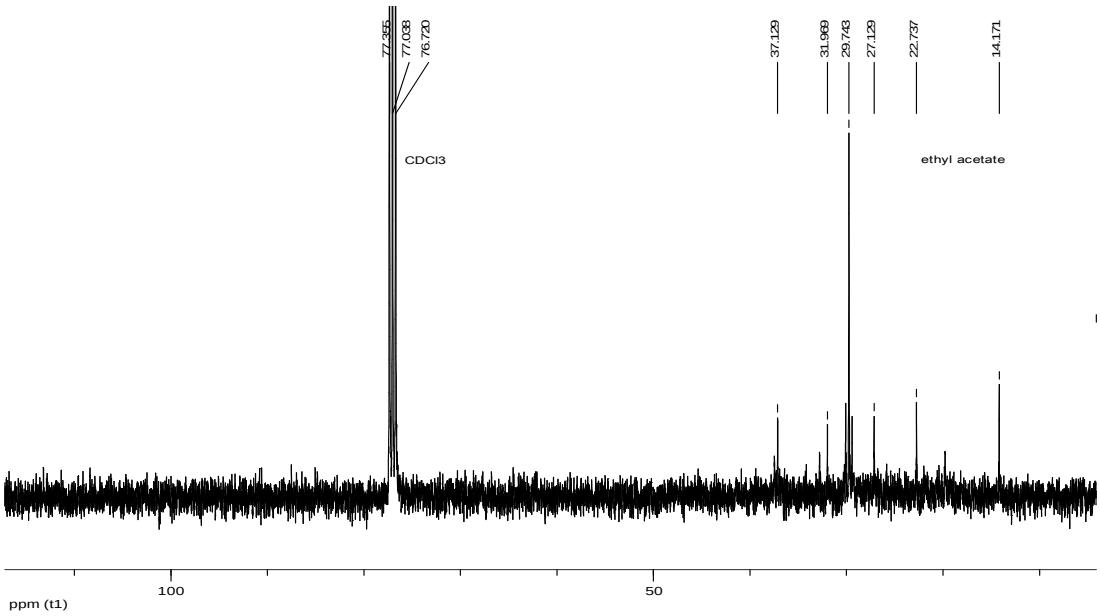


(B)

Appendix 9: (A) ^{1}H and (B) ^{13}C NMR spectra of 48h reaction product of WIM-1 catalyst at 100 ^{o}C

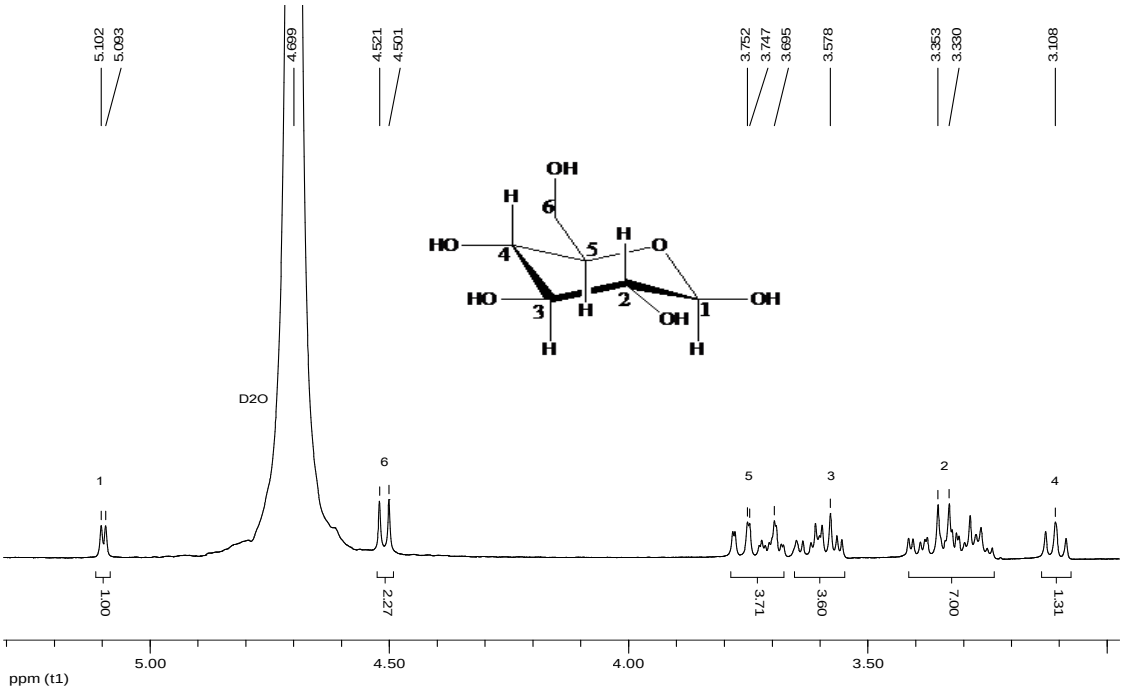


(A)

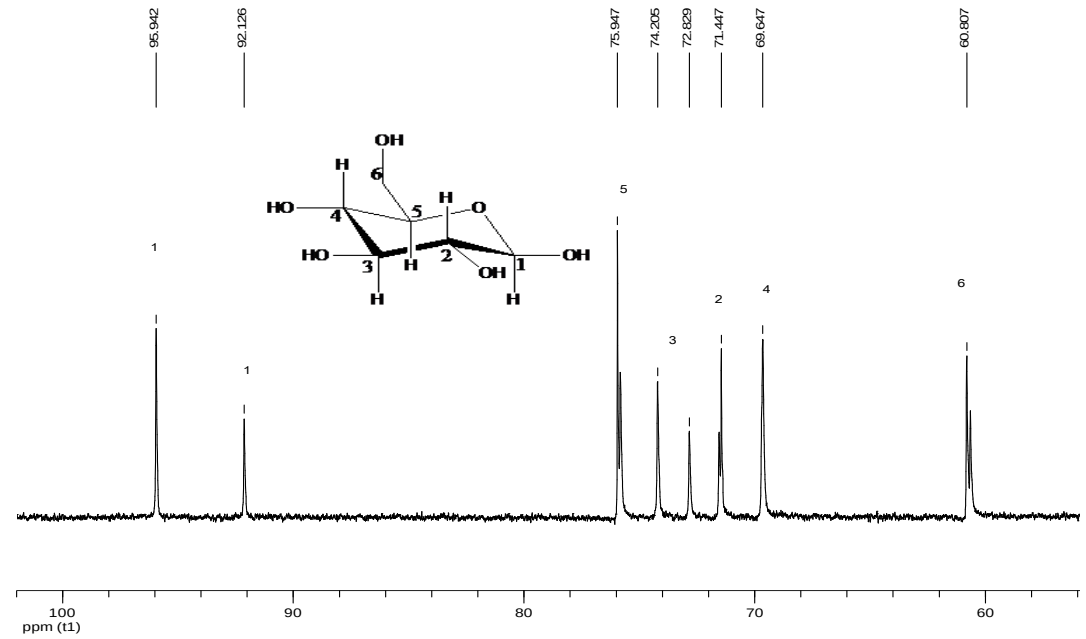


(B)

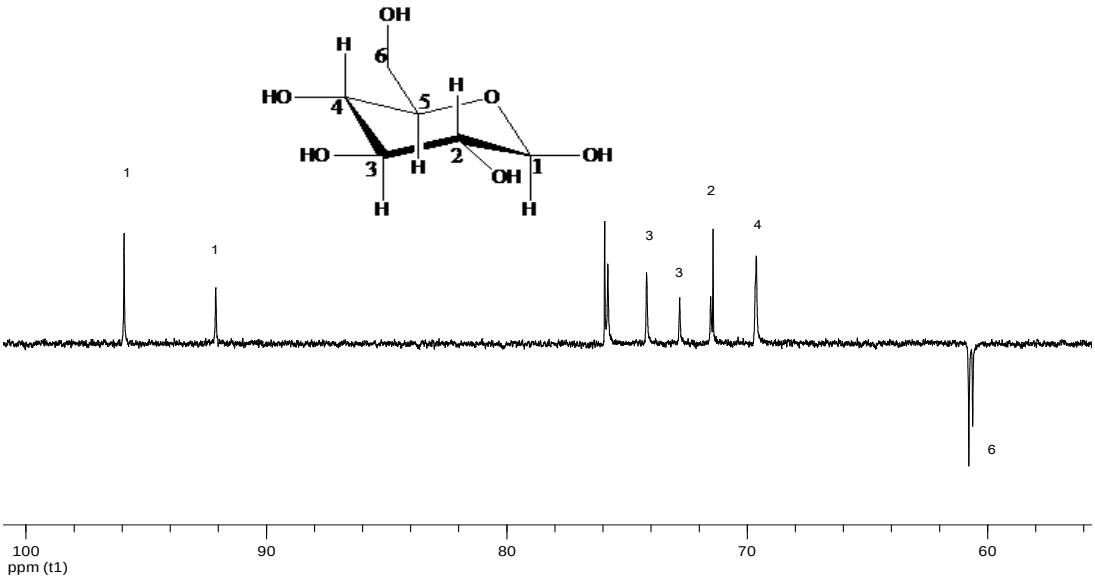
Appendix 10: (A) ^{1}H, (B) ^{13}C NMR and (C) DEPT spectra of 48h reaction residue of WIM-7 catalyst at 100 ^{o}C



(A)

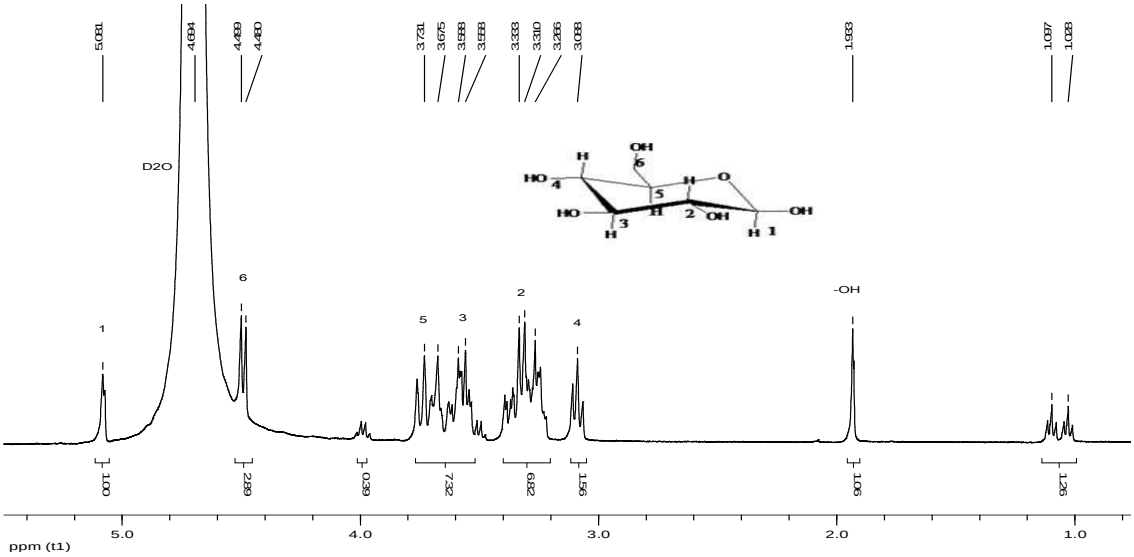

95.942
92.126
75.947
74.205
72.829
71.447
69.647
60.807
OH
H
6
HO
4
5
H
O
HO
3
H
2
OH
1
OH
H
H
1
1
5
3
2
4
6
100
90
80
70
60
ppm (t1)

(B)

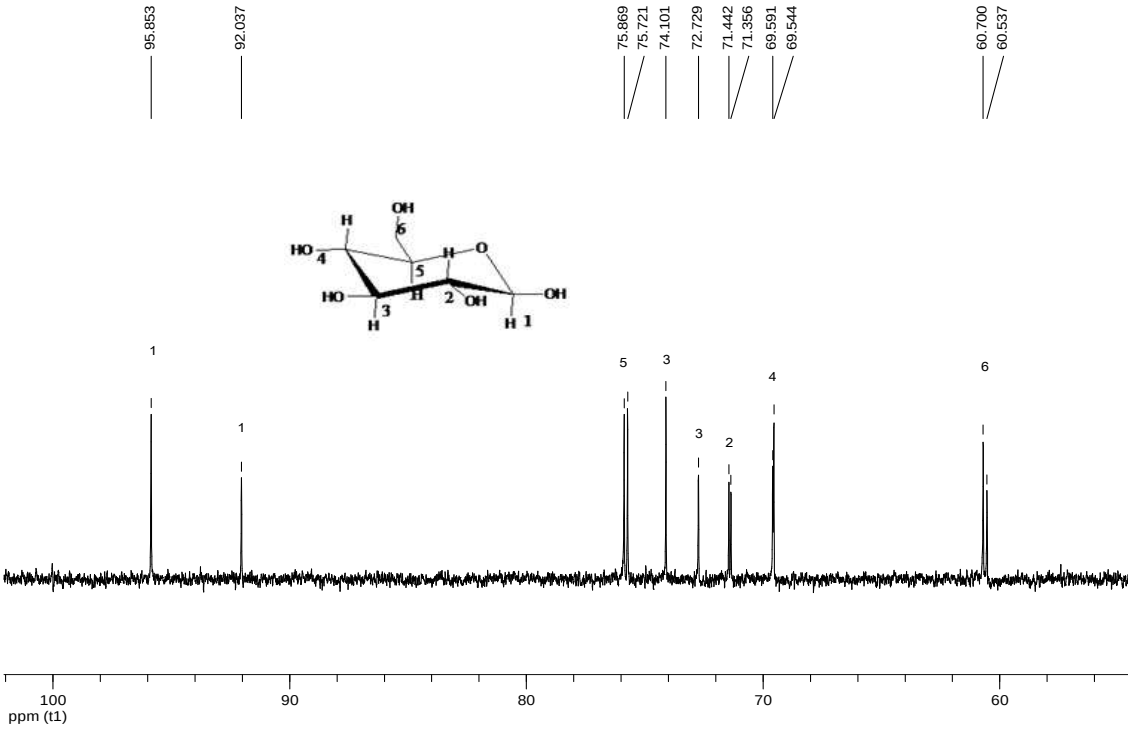

OH
H
6
HO
4
5
H
O
HO
3
H
2
OH
1
OH
H
H
1
1
3
3
2
4
6
100
90
80
70
60
ppm (t1)

(C)

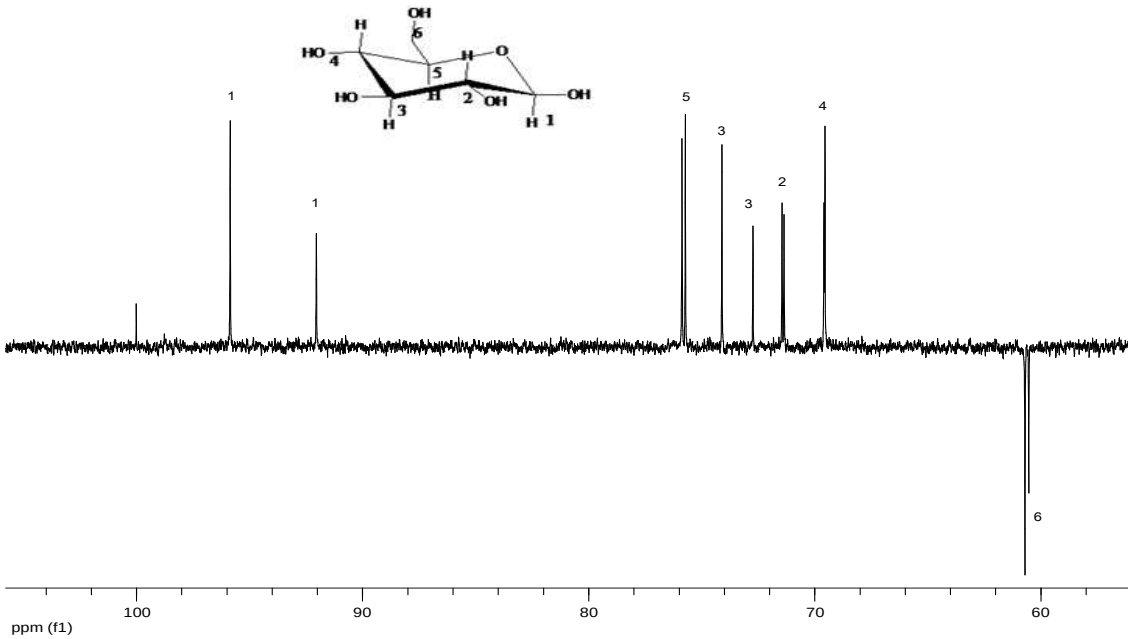
Appendix 11: (A) ^{1}H, (B) ^{13}C NMR and (C) DEPT spectra of 24 h reaction residue of SAPO 1.5T catalyst at 120 ^{o}C



(A)

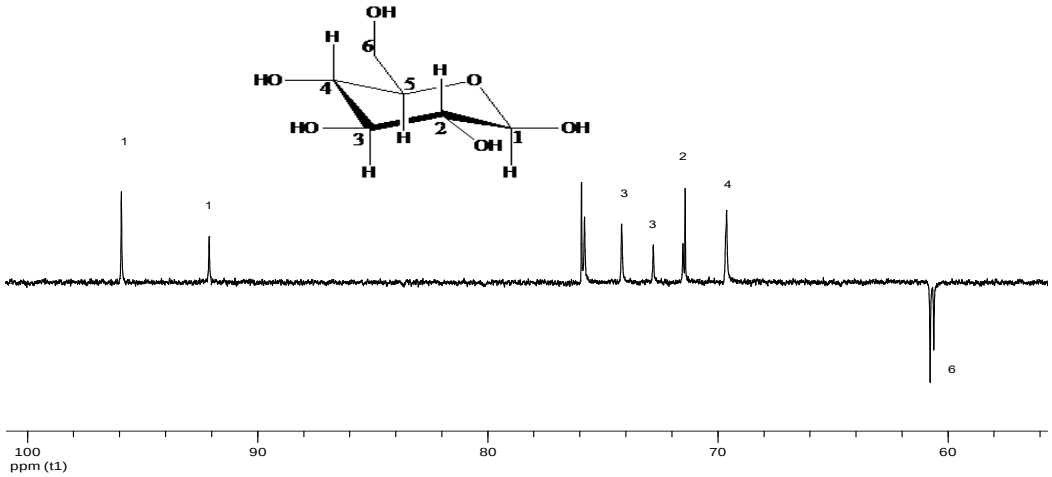


(B)

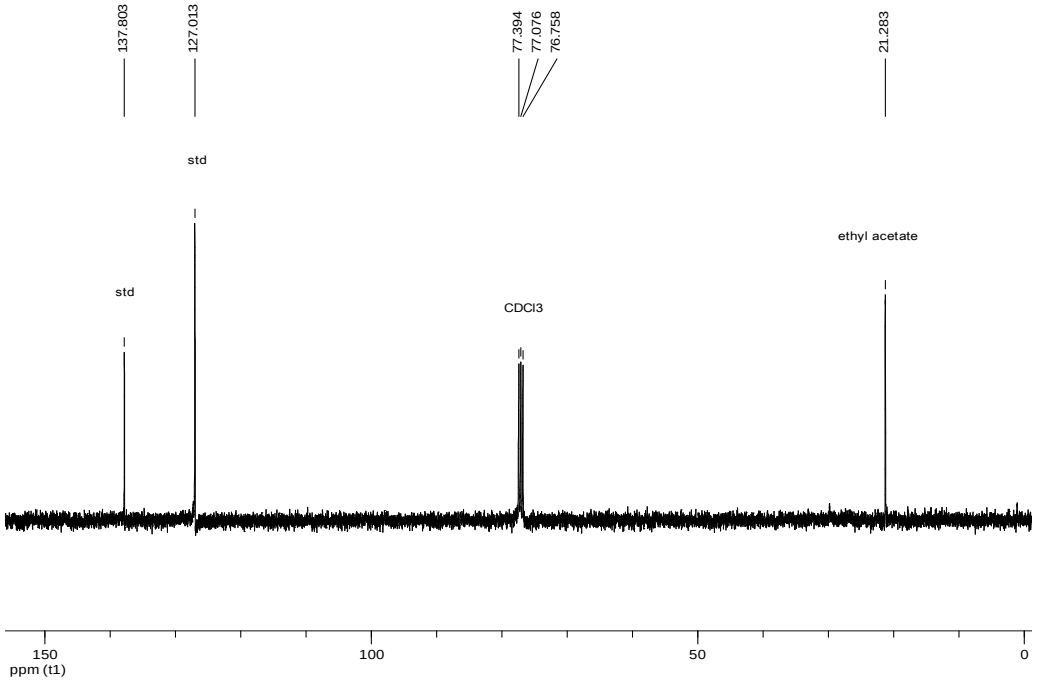


(C)

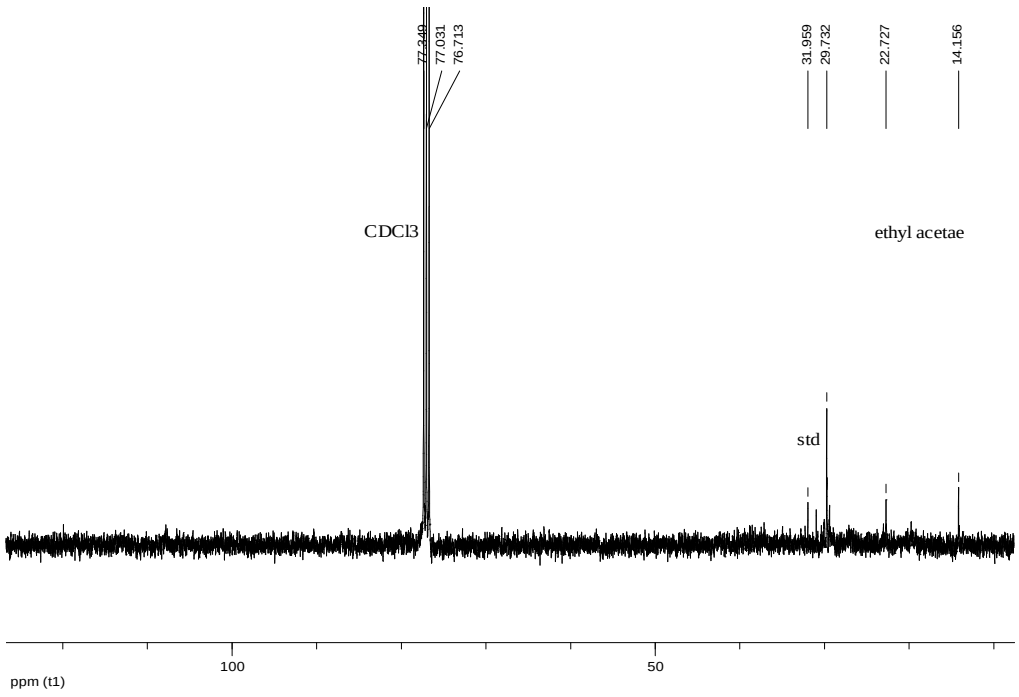
Appendix 12: DEPT spectra of 24 h reaction residue of SAPO 1.5B at 120 ^{o}C



Appendix 13: ^{13}C NMR spectra of 6 h biphasic reaction product of MOR-CBV-21A catalyst at 150 ^{o}C (A) in the presence of NaCl and (B) in the absence of NaCl



(A)



(B)