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RESEARCH ARTICLES

Thermochemical Property Predictions in Biomass Transformation to Fuel Components and Value-added Chemicals

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Abstract: Biomass transformation to fuel and platform chemicals is of an immense interest in the world. The thermochemical data for various reactions involved during biomass transformations to fuel components, fuels and platform chemicals have been investigated using highly accurate Gaussian-4 (G-4) method. Glucose to 5-hydroxymethyl furfural (5-HMF) conversion is a two-step pathway, where first step, glucose isomerization to fructose is highly endothermic with high activation energies. 5-HMF upgradation can be carried through hydrogenation, oxidation, condensation and rehydration. Upgradation of HMF to fuel and value-added chemicals (VAC) is an industrially important process that can reduce the demand of petrochemical based products. Thermochemical calculations predict the hydrogenation of 5-HMF to 2,5 dimethyl furan (2,5 DMF) is feasible and follow either pathways with dihydroxy methyl furan (DHMF) and methyl furan (MF) as intermediates. The total Gibb's free energy difference for the 5-HMF transformation to 2,5 DMF is highly exothermic. The condensation, rehydration and oxidation reactions of 5-HMF also predicted to be feasible and highly exothermic in nature. That can have potential application in industrial processes. Ethanol is mixed with petrol to run the vehicle on reduced fuel. Ethanol can be obtained from glucose following glycolysis pathway, breaking C-6 sugar to two C-3 sugars. Glyceraldehyde and pyruvic acid are the intermediates in the glycolysis cycle with positive Gibbs free energy change, hence requiring high temperature.

Keywords: Thermochemical calculation, Value added chemicals, Fuels

1. Introduction

High demand and irrational utilization of fossil fuel led to its depletion and increase in the concentration of carbon dioxide responsible for global warming as it absorbs infrared radiation through the bending mode of CO_2 [1,2]. Hence, conversion of biomass, a carbon neutral renewable feedstock, to fuel and chemical intermediates is an immediate requirement for a sustainable future. A series of reactions (such as hydrolysis of extensively hydrogen bonded cellulose to glucose, glucose isomerization to fructose, fructose dehydration to 5-hydroxymethyl furfural (5-HMF) a

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platform chemical and HMF transformation to the various industrially important chemicals) are required for biomass transformation to fuel components or chemically important intermediates [3–10]. The conversion of glucose, derived from biomass, to chemical intermediates and fuel is the challenging task. The efficient transformation of these chemicals required design of new catalyst with better efficiency, understanding of the molecular pathways, their kinetics and thermochemistry of these chemicals [11,12]. The thermochemistry of the reactions involved in glucose transformation to varied chemicals and fuels can be studied by employing computational chemistry with high molecular orbital theory.

The reported literature showed the conformational analysis of the carbohydrates and studies on their structural parameters and interaction energies with the hydrocarbons [13–18]. Xiang and Chang reported the kinetic modelling of glucose conversion to levulinic acid at different acidic conditions [19,20]. In the literature, the conversion of glucose to HMF has been reported using metal chloride, $CrCl_2$ in ILs, but lacks the actual energetics of the reaction [21,22]. In the earlier literature, the HMF conversion to value added chemicals and fuels to replace the petroleum based chemicals with 2,5-dimethyl furan has been studied [23–25]. Verevkin et al. reported the experimental as well as theoretical thermochemical data of HMF in terms of it molar enthalpy of formation, using the combustion calorimeter, differential scanning calorimetry and temperature dependence from the transpiration method [26]. Reported literature lacks the study on thermochemistry data for glucose to HMF transformation, HMF upgradation to fuel and platform chemicals such as levulinic acid, formic acid and ethanol [27,28]. To understand further the key features of the glucose transformation to the feasibility of the glucose dehydration to HMF, production of fuel from HMF, monomers for polymer industry and solvents detailed thermochemical investigations are necessary.

Henceforth, in this study, the accurate thermochemical data for the conversion of glucose to fructose following Lobry de Bruyn Van Ekenstein rearrangement and fructose to HMF transformation with subsequent release of three molecules of water with the variation in temperature has been studied with G4 high quantum mechanical method. Moreover, the feasibility of HMF conversion to varied chemical intermediates and fuels by condensation, rehydration, and hydrogenation method has been studied.

2. Experimental Section

Theoretical Methods

Density Functional Theory (DFT) is quantum mechanical method to study the electronic structure of the molecule [29]. All the molecular geometries were optimized using DFT employed with B3LYP level at 6-31G basis set to find out the conformer with the minimum energy. Then the refinement in the geometry and energy calculation at gas phase by single energy calculations were performed using Gaussian-4 (G-4) theory at different temperatures [30]. G-4 theory is composite theory which calculate the total energy of the molecule using sequence of well-defined molecular orbital calculations. The energy calculation using G-4 theory deviates from the experimental value by a factor of 0.83 kcal/mol on the 454 energies in the G3/05 test set comprising of enthalpy of formation, electron affinity, ionization energies, hydrogen bond energies and proton affinities [31]. All the calculations were performed using Gaussian-09 program package [32]. The enthalpy and free energy change of the reaction were calculated using the Equations (1& 2) given below:

$$\Delta rE = \sum \Delta Eproduct - \sum \Delta Ereactant \quad (1)$$

$$\Delta rH = \sum \Delta Hproduct - \sum \Delta Hreactant \quad (2)$$

$$\Delta rG = \sum \Delta Gproduct - \sum \Delta Greactant \quad (3)$$

where $\Delta rE, \Delta rH, \Delta rG$ are total energy, enthalpy and free energy change for a reaction, $\Delta\mathrm{Eproduct}, \Delta\mathrm{Hproduct}, \Delta Gproduct$ are total energy, enthalpy and free energy change for the products and $\Delta\mathrm{Ereactant}, \Delta\mathrm{Hreactant}, \Delta Greactant$ are total energy, enthalpy and free energy change for the reactants respectively.

3. Results and Discussion

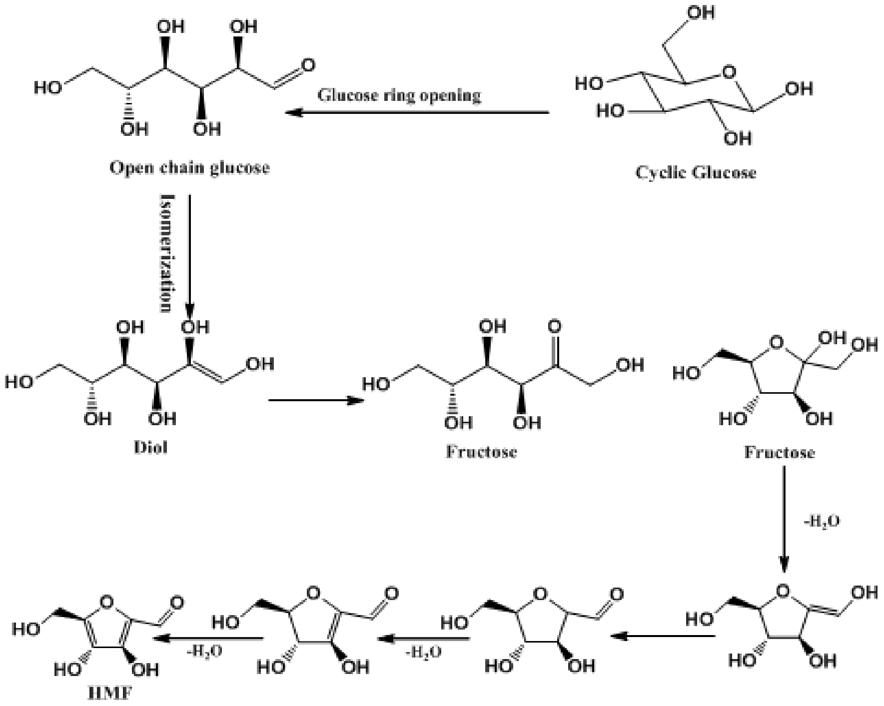
Glucose transformation to HMF occurs through two pathways (i) glucose isomerization to fructose and (ii) fructose dehydration to HMF as shown in Scheme 1. All the optimized geometries of molecules are shown in Figure 1. The enthalpy and free energy of reactions are calculated for the following reactions (i) ring opening of glucose to open chain, (ii) isomerization of glucose to diol following Lobry de Bruyn–van Ekenstein rearrangement, (iii) diol conversion to fructose, (iv) fructose cyclization (v) removal of a molecule of water from fructose to enol-intermediate, (vi) enol tautomerization, (vii) release of the second water molecule and (viii) release of the third water molecule to form HMF.

3.1 Glucose Isomerization to Fructose

The enthalpy and free energy changes for the reactions involved in glucose conversion to fructose are shown in Table 1. The change in enthalpy and free energy for glucose ring opening at 298 K are 9.95 kcal/mol and 7.47 kcal/mol respectively. The effect of temperature from the

Table 1 revealed that increasing the temperature favored the glucose ring opening since, at high temperature, the reaction ΔG value is decreasing resulting in the reaction to be feasible. The enthalpy and free energy change glucose to diol intermediate undergoing keto-enol tautomerism following the Lobry de Bruyn–van Ekenstein rearrangement was found to be 3.88 kcal/mol and 3.45 kcal/mol respectively. The reaction is endothermic, diol so formed becomes unstable at higher temperature, hence change in free energy increases on increasing the temperature.

The transformation of relatively less stable diol intermediate to open chain fructose was found to be exothermic with enthalpy and free energy change of –8.86 kcal/mol and –9.46 kcal/mol respectively. Cyclization of fructose was found to exothermic reaction but with less enthalpy and free energy values –1.81 kcal/mol and –0.51 kcal/mol respectively as compared to the diol to fructose transformation reaction. At higher temperature, free energy change values become positive due to the entropic effects.



Scheme 1. Schematic diagram for glucose conversion to HMF.

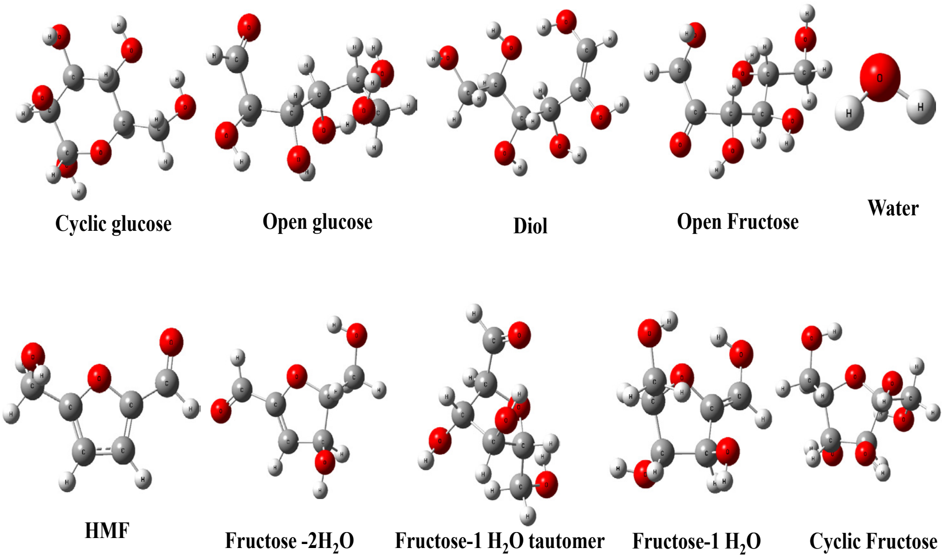


Figure 1. Optimized geometries of all intermediates, reactants and products for glucose conversion to HMF.

Table 1. Thermochemistry (kcal/mol) for glucose isomerization to fructose.

Reaction T (°C)	Glucose ring opening			Tautomerization to diol			Fructose from diol			Cyclization of fructose		
	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG
25	9.95	9.95	7.47	3.45	3.45	3.88	–8.86	–8.86	–9.46	–1.81	–1.81	–0.51
50	10.00	10.00	7.28	3.47	3.47	3.90	–8.87	–8.87	–9.51	–1.84	–1.84	–0.40
75	10.05	10.05	7.06	3.49	3.49	3.94	–8.89	–8.89	–9.56	–1.87	–1.87	–0.29
100	10.10	10.10	6.85	3.51	3.51	3.97	–8.90	–8.90	–9.60	–1.90	–1.90	–0.18
125	10.14	10.14	6.63	3.53	3.53	4.00	–8.92	–8.92	–9.65	–1.93	–1.93	–0.06
150	10.18	10.18	6.41	3.54	3.54	4.03	–8.93	–8.93	–9.70	–1.95	–1.95	0.05

ΔE, Total energy change for reaction, ΔH, enthalpy change for the reaction and ΔG, Gibb's free energy for the reaction calculated at different temperatures following equationns 1, 2 & 3

3.2 Fructose Dehydration to HMF

Removal of first molecule of water from fructose to enol intermediate is highly endothermic reaction with values of enthalpy and free energy change as 18.73 kcal/mol and 7.07 kcal/mol respectively at temperature of 25 °C as reported in Table 2. The temperature effect shows that the reaction is favored at high temperatures. The endothermicity of first dehydration step can be attributed to the bond breaking and forming during the reaction. During the release of one water molecule from fructose, C-C and C-O bonds break, and in the product C-C single bond gets transformed to (C=C) double bond, also there is formation of O-H bond in the water molecule liberated. The transformation of single C-C bond to double C=C bond requires energy that is responsible for the endothermicity of the first dehydration step. Furthermore, the endothermicity to the reaction is contributed from the disruption of intramolecular hydrogen bonding during transformation to fructose intermediate with a loss of one molecule of water. The tautomerization of enol intermediate to the aldehydic form is an exothermic process with an enthalpy and free energy change of –6.94 kcal/mol and –6.47 kcal/mol respectively as shown in Table 2.

The effect of temperature on the reaction suggests that at higher temperatures the reaction is disfavored with slight increase in the values of enthalpy and free energy change. The feasibility or exothermicity of tautomerization can be explained based on greater stability of aldehydic form compared to enol intermediate, which is given by the bond energies of the reactant and products. In enol intermediates, associated bonds are C=C, C–O an O–H having sum of bond energies as 347 kcal/mol whereas aldehyde form has C–H, C–C, and C=O bonds with sum of bond energies equal to 359 kcal/mol. The aldehydic form is more stable with the energy value of 12 kcal/mol. The removal of second water molecule from the aldehydic form is also an endothermic reaction similar to the first dehydration step. The change in enthalpy and free energy are 7.7 kcal/mol and –4.3 kcal/mol respectively at 25 °C. The liberation of the second water molecule is less endothermic than the liberation of the first molecule of water due to the conjugation between the C=C and C=O bond after second water molecule liberation. The second dehydration being endothermic, it is favorable at higher temperatures as the entropy factors determine the reaction results from the stabilization of product because of the conjugation between C=C and C=O bonds. Unlike, first two dehydration steps, third dehydration step is an exothermic with enthalpy and free energy change as –7.66 kcal/mol and –18.83 kcal/mol respectively at 25 °C. From Table 2, it can be concluded that the reaction is favorable at higher temperatures.

3.3 HMF Hydrogenation to 2,5-dimethyl Furan

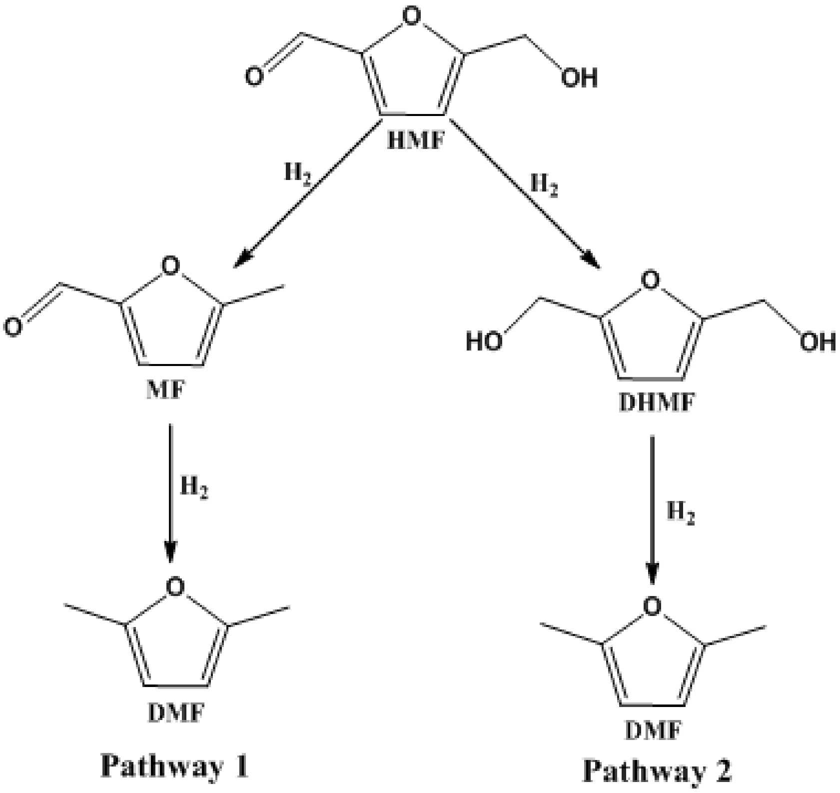
Scheme 2 shows predicted pathways for HMF hydrogenation to 2,5-dimethyl furan (i) methyl furan as an intermediate and (ii) dihydroxy methyl furan as an intermediate. All the optimized structures are shown in Figure 2. Dimethyl furan can be used as a fuel as it has very high energy density 31.5 MJ/L and octane number 119 [33]. Apart from being a fuel component it can be used as a lubricant because of its good antifriction and antiwear properties [34].

HMF hydrogenation to 2,5 dimethyl furan can be proceeded through two pathways as shown in Scheme 2. (i) HMF can undergo pathway 1, first hydrogenated to dihydroxy methyl furan with an enthalpy and free energy change values of –43.24 kcal/mol and –8.99 kcal/mol respectively, as listed in Table 3. Di-hydroxymethyl furan further hydrogenates to 2,5-dimethyl furan with

Table 2. Thermochemistry (kcal/mol) for fructose dehydration to HMF.

Reaction T (°C)	First dehydration			Enol tautomerization			Second dehydration			Third dehydration		
	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG
25	18.14	18.73	7.07	–6.94	–6.94	–6.47	7.10	7.70	–4.3	–8.25	–7.66	–18.83
50	18.15	18.79	6.09	–6.98	–6.98	–6.43	7.128	7.77	–5.34	–8.27	–7.63	–19.75
75	18.155	18.84	5.11	–7.02	–7.02	–6.38	7.137	7.82	–6.36	–8.30	–7.61	–20.69
100	18.14	18.88	4.12	–7.06	–7.06	–6.33	7.136	7.87	–7.38	–8.33	–7.59	–21.63
125	18.12	18.91	3.13	–7.10	–7.10	–6.28	7.12	7.91	–8.41	–8.37	–7.58	–22.57
150	18.09	18.93	2.14	–7.13	–7.14	–6.23	7.10	7.94	–9.43	–8.42	–7.58	–23.51

ΔE, Total energy change for reaction, ΔH, enthalpy change for the reaction and ΔG, Gibb's free energy for the reaction calculated at different temperatures following equtaion 1, 2 & 3



Scheme 2. Different conversion routes for HMF to DMF transformation.

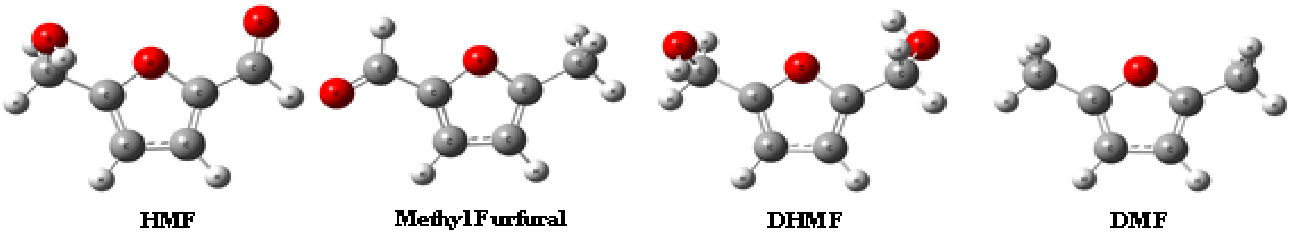


Figure 2. Optimized structures for HMF to DMF transformation.

an enthalpy change of –157.80 kcal/mol and free energy change of –175.23 kcal/mol. (ii) During pathway 2, HMF is first hydrogenated to methyl furan with an enthalpy and free energy change of –88.58 kcal/mol and –98.04 kcal/mol respectively. Further, hydrogenation of methyl furan to DMF have enthalpy and free energy change values of –112.46 kcal/mol and –86.17 kcal/mol respectively. From the summation of free energy change values, it can be concluded that pathway 1 & 2 are of equal energy.

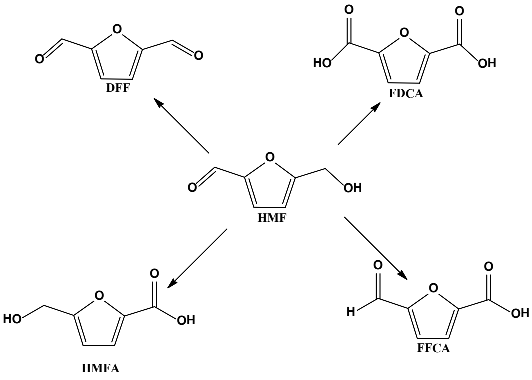
Table 3. Thermochemistry (kcal/mol) for different pathways of HMF hydrogenation to DMF.

Reactions	Thermochemical Parameters		
	ΔE	**ΔH**	**ΔG**
HMF to DHMF	–40.76	–43.24	–8.99
HMF to MF	–88.58	–88.58	–98.04
DHMF to DMF	–157.80	–157.80	–175.23
MF to DMF	–109.99	–112.46	–86.17

ΔE, Total energy change for reaction, ΔH, enthalpy change for the reaction and ΔG, Gibb's free energy for the reaction calculated at room temperature following equation 1, 2 & 3

3.4 HMF Oxidation to Value Added Chemicals

From Scheme 3, HMF can be oxidized to various chemically important intermediate.



Scheme 3. Schematic representation for HMF oxidation.

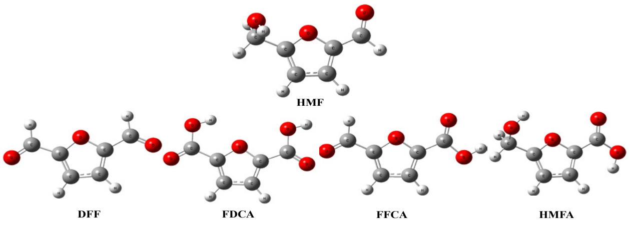


Figure 3. Optimized geometries of molecules obtained from HMF oxidation.

All the optimized structures are shown in Figure 3. HMF oxidized to 5-formylfuran-2-carboxylic acid with an enthalpy and free energy change of –130.27 kcal/mol and –130.01 kcal/mol respectively. The transformation of HMF to FFCA is an exothermic reaction and the predicted thermochemical parameters are shown in Table 4. Oxidation of HMF to furan dicarboxylic acid (FDCA), an intermediate in the polymer industry is also an exothermic reaction with enthalpy change and free energy value equal to –203.07 kcal/mol and –197.22 kcal/mol respectively. The oxidation of HMF to di formyl furan and 5-hydroxymethyl furoic acid are exothermic in nature with enthalpy and free energy change values of –55.91 kcal/mol & –60.75 kcal/mol and –69.92 kcal/mol & –64.85 kcal/mol respectively. All the oxidation reactions are feasible and highly exothermic in nature, hence, can be applied in an industrial process.

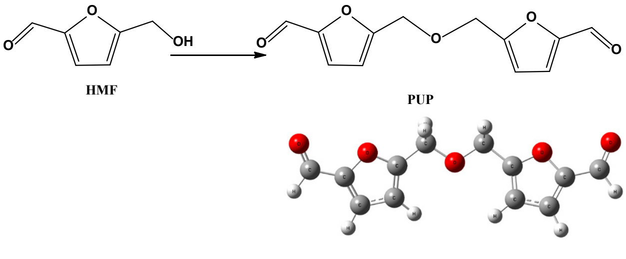
Table 4. Thermochemistry (kcal/mol) for HMF oxidation.

Reactions	Thermochemical Parameters		
	ΔE	**ΔH**	**ΔG**
HMF to FFCA	–130.27	–130.26	–130.01
HMF to FDCA	–202.78	–203.07	–197.22
HMF to HMFA	–69.62	–69.92	–64.85
HMF to DFF	–56.21	–55.91	–60.75

ΔE, Total energy change for reaction, ΔH, enthalpy change for the reaction and ΔG, Gibb's free energy for the reaction calculated at room temperature following equation 1, 2 & 3

3.5 HMF Dimerization to Bio-based Polyurethane bis-5(Methylfurfuryl) Ether

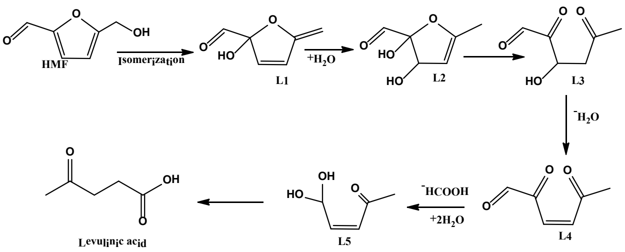
Condensation of two molecules of HMF results in the synthesis of bis-5(methylfurfuryl) ether as shown in Scheme 4, which allows the preparation of a rigid polyurethane foam with improved flame hazard properties. Dimerization of HMF is an exothermic reaction with enthalpy value of –1.82 kcal/mol and free energy value as –1.15 kcal /mol [35].



Scheme 4. Schematic and optimized geometry for PUP.

3.6 5-hydroxymethylfurfural Rehydration to Levulinic acid

HMF obtained from the glucose dehydration can be further rehydrated to the levulinic acid (LA) and formic acid (FA) as shown in Scheme 5 and the optimized structures are depicted in Figure 4.



Scheme 5. Schematic representation of HMF rehydration to levulinic acid.

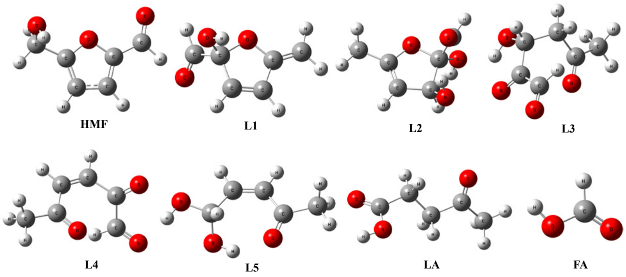


Figure 4. Optimized geometries of molecules obtained from HMF rehydration to levulinic acid.

LA is isomerized to L1 with negative enthalpy and free energy value of –6.72 kcal/mol and –7.00 kcal/mol respectively. The isomerization is an exothermic reaction favorable at lower temperatures. L1 hydration to L2 has a negative enthalpy change –8.3 kcal/mol but positive free energy change 2.68 kcal/mol as depicted in Table 5. This showed that L2 is less favorable over L1 due to the destruction of resonance in L2 which was present in L1. Whereas, L2 can be easily converted to L3 with negative values of enthalpy and free energy change of –3.40 kcal/mol and –4.85 kcal/mol respectively. L3 dehydration to L4 is an endothermic reaction feasible at high temperatures with enthalpy and free energy change value of 13.5 kcal/mol and 1.84 kcal/mol respectively. L4 rehydrated to L5 and formic acid with enthalpy and free energy change value of –15.56 kcal/mol and –5.02 kcal/mol respectively. L5 undergoes enol isomerization to yield LA with high negative enthalpy change and free energy values –27.99 kcal/mol and –29.57 kcal/mol respectively.

Table 5. Thermochemistry (kcal/mol) for HMF rehydration to Levulinic acid

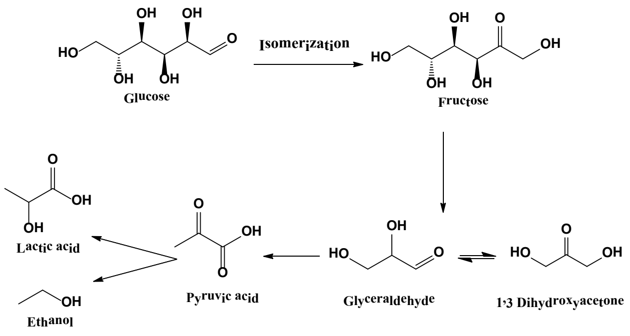
Reactions	**Thermochemical Parameters**		
	ΔE	**ΔH**	**ΔG**
HMF isomerization to L1	–6.72	–6.72	–7.00
L1 hydration to L2	–7.70	–8.30	2.68
L2 conversion to L3	–3.40	–3.40	–4.85
L3 dehydration to L4	12.90	13.50	1.84
L4 hydration to L5 and formic acid	–14.97	–15.56	–5.02
L5 to Levulinic acid	–27.99	–27.99	–29.57

ΔE, Total energy change for reaction, ΔH, enthalpy change for the reaction and ΔG, Gibb's free energy for the reaction calculated at room temperature following equation 1, 2 & 3

3.7 Ethanol as a Fuel from Cellulosic Glucose

Ethanol can be used as additive to the fuel and also considered as renewable fuel obtained from cellulose derived glucose with heat content of 26.8 MJ/Kg and cetane number 5-8 [36]. Scheme 6 shows the different reaction pathways for the conversion of glucose to ethanol glyceraldehyde and pyruvic acid as intermediates. Optimized geometries of all the molecules are depicted in Figure 5. From Table 6, it can be explained that glucose isomerization to fructose is an exothermic process with –5.31 kcal/mol and –5.47 kcal/mol for enthalpy and free energy change respectively.

Fructose is a six-carbon sugar that can be converted into two 3 carbon sugar called glyceraldehyde with enthalpy and free energy change values of 20.13 kcal/mol and 5.82 kcal/mol respectively. The reaction is an endothermic high temperature catalytic reaction. Glyceraldehyde obtained from fructose remains in equilibrium with the dihydroxyacetone with enthalpy and free energy change values of –5.04 kcal/mol and –4.86 kcal/mol respectively. Glyceraldehyde undergoes oxidation to yield pyruvic acid, the reaction is exothermic with enthalpy and free energy change values of –6.56 kcal/mol and –15.41 kcal/mol respectively. Pyruvic acid is an important intermediate that can convert to lactic acid or ethanol. The reactions are exothermic with enthalpy and free energy values of –19.04 kcal/mol & –10.08 kcal/mol and –25.50 kcal/mol & –26.81 kcal/mol respectively for hydrogenation of pyruvic acid to lactic acid and pyruvic acid to ethanol with the loss of one molecule of carbon dioxide.



Scheme 6. Schematic for glucose conversion to ethanol.

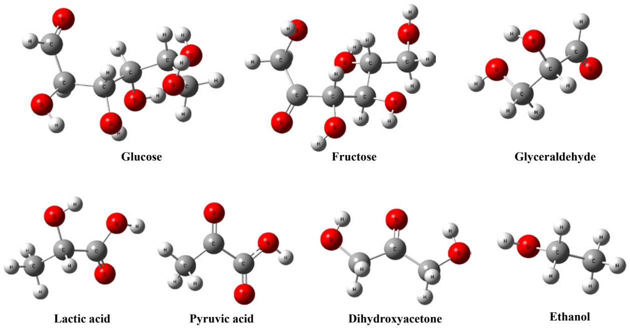


Figure 5. Optimized structures of intermediates for glucose conversion to ethanol

Table 6. Thermochemistry (kcal/mol) for glucose conversion to ethanol

Reactions	**Thermochemical Parameters**		
	ΔE	**ΔH**	**ΔG**
Glucose isomerization to Fructose	–5.31	–5.31	–5.47
Fructose to Glyceraldehyde	19.53	20.13	5.82
Glyceraldehyde isomerization to Dihydroxyacetone	–5.04	–5.04	–4.86
Glyceraldehyde to Pyruvic acid	–7.15	–6.56	–15.41
Pyruvic acid to Lactic acid	–18.45	–19.04	–10.08
Pyruvic acid to Ethanol	–25.50	–25.50	–26.81

ΔE, Total energy change for reaction, ΔH, enthalpy change for the reaction and ΔG, Gibb's free energy for the reaction calculated at room temperature following equation 1, 2 & 3

4. Conclusions

In this study, the thermochemical conversion of glucose to HMF and HMF upgradation to value added chemicals and fuels have been studied using Gaussian-4 or G-4 theory. Isomerization of glucose to fructose following Lobry de Bruyn–van Ekenstein rearrangement through thermodynamically unstable diol intermediate is an endothermic reaction (ΔG 3-10 kcal/mol). During fructose dehydration to HMF, first two dehydration steps are endothermic (ΔG 2-7 kcal/mol) and are favourable at high temperatures, whereas, liberation of third water molecule is an exothermic step (ΔG –18 to –23 kcal/mol) due to the formation stable product HMF. HMF conversion to DMF follows two pathways, transformation of HMF to DMF through DHMF intermediate is a fovoured over the pathway with methyl furfural intermediate. Oxidation of HMF to FFCA, FDCA, DFF, and HMFA is favourable with negative free energies (ΔG –56 to –203 kcal/mol) values for each reaction. Industrially important dimerization of HMF to polyurethane bis-5(methylfurfuryl) ether has negative ΔG value (1.82 kcal/mol) and hence, is thermochemically viable process. Rehydration of HMF to levulinic acid and formic acid is a multistep process with first hydration followed by dehydration steps are endothermic (ΔG 1-6 kcal/mol) in nature, whereas all other reactions are exothermic in nature (ΔG –4 to –29 kcal/mol). Glucose conversion to ethanol is an exothermic industrially feasible reaction (ΔG –4 to –26 kcal/mol). The energy calculations predict the transformation of biomass derived glucose to fuel and value added chemicals is feasible and can be explored industrially.

Conflict of Interest

There is no conflict of interest.

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