



Mechanism of glucose conversion in supercritical water by DFT study



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ARTICLE INFO

Article history:

Received 6 September 2015

Accepted 23 February 2016

Available online 15 March 2016

Keywords:

Glucose conversion

Supercritical water

Density function theory (DFT)

ABSTRACT

Using density function theory (DFT) simulations with B3LYP/AGU-cc-pVDZ level of theory, six chemical reaction pathways of glucose decomposition in supercritical water were proposed to explore the formation mechanism of some main outcomes (levoglucosan, 5-hydroxymethylfurfural, hydroxylacetaldehyde, erythrose, glyceraldehyde and fructose). In addition, seven potential dehydration ways in glucose were investigated with and without the assistance of water molecule. All dehydration reactions are accelerated when water molecules take part in the reaction, because it can effectively lower the energy barrier of dehydration reaction. In supercritical water surrounding with assistant of water molecule, pathways 3 and 4 are preferred routes of glucose conversion to hydroxylacetaldehyde and erythrose with the lowest energy barrier of 127 kJ/mol. While a higher energy barrier (163 kJ/mol) is required to form glyceraldehyde and fructose in pathways 5 and 6. Levoglucosan and 5-hydroxymethylfurfural are hard to generate during this chemical processes because of their higher energy barrier without water participating in. It seems like that water molecule acts as a magic catalyst that can transfer hydrogen atom in dehydrations, keto-enol tautomerization and structure rearrangement, which reducing the distance of hydrogen atom moving, result in reducing these reactions energy barriers dramatically. The computational results open a window to produce hydroxylacetaldehyde and erythrose in theory. Moreover, it sheds some light on the various proportions of different products in conversion of glucose in supercritical water, as well as suggesting concrete reaction pathways to form these main products, contributing to the elaboration of the mechanism of glucose conversion and cellulose decomposition from a molecule level.

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1. Introduction

The widely distributed and renewable biomass is considered as the fourth largest source of energy and contributing to about 14% of primary energy consumption of the whole world [1]. There are several methods to convert biomass into fuel, such as biochemical conversion and thermochemical conversion. Whereas, extensive research has been devoted to conventional technics like pyrolysis and gasification. Little interest was attracted to other special ways (ions liquid, supercritical water, hydrogenation et.) to use biomass energy, among which gasification in supercritical water is a promising technology to gasify biomass with high moisture content. Using water as a reaction medium instead of needing to dry the feedstock could allow a faster reaction rate. The gasification outcomes are mainly gases like hydrogen, carbon dioxide, carbon monoxide, and

C1–C4 hydrocarbons [2,3]. Similarly to conventional gasification processes, some oil and char reaction products are also produced. Therefore, it is also considered as an effective way to utilize biomass energy. Cellulose is the main composition of the biomass, so it is of importance to study on the mechanism of cellulose decomposition under supercritical water condition (SCWC).

The supercritical water gasification reaction occurs in an aqueous fluid phase under the condition of the critical point of water ($T_c = 374^\circ\text{C}$, $P_c = 21.9\text{ MPa}$) being exceeded [4]. Large numbers of efforts have been spent on cellulose decomposition experiments under SCWC, focusing on the variation of exterior conditions and resulting of products of various gas, and obtaining kinetic parameters through kinetic models of gases products formation [5]. Decomposition experiments of microcrystalline cellulose were conducted in subcritical and supercritical water in ref [6], which indicated that hydrolysis products are mainly obtained at 400°C , and aqueous decomposition products of glucose are obtained at a lower temperature. Their results also suggested that cellulose hydrolysis at high temperature takes place with dissolution in

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water. A similar experiment was conducted by Sasaki et al. [7], in which the main outcomes of cellulose conversion were hydrolysis products, aqueous degradation outcomes of glucose, such as fructose, erythrose, glycolaldehyde, etc., and some undetected species. Another study [8] revealed that supercritical water treatment can overcome the difficulties in hydrolyzing cellulose, which may due to that an accessibility of water nears cellulose molecules has significant effect on these chemical conversion. Many inner and outer effects were investigated containing the temperature, pressure, residence time, biomass types, biomass particle size and catalysts [3] and the results showed that the gas yield of biomass gasification in supercritical water is sensitive to some of these parameters.

However, there were few researches addressing the mechanism of what and how these products are formed under SCWC. The glucose is a monomer unit of cellulose and can be generated from cellulose via hydrothermal reactions [8], under which cellulose can also convert to useful chemical products that can be recognized as a candidate for suitable sustainable feed stock. Interestingly, similar products were obtained through gasification of glucose under SCWC [9]. A detailed description can be found in the ref [5], where with an extremely short residence, glucose decomposition products were fructose, erythrose, glyceraldehyde, 1,6-anhydroglucose, dihydroxyacetone, pyruvaldehyde, and small amounts of 5-hydroxymethylfurfural (5-HMF). A kinetic model was also established to elucidate these outcomes formation and gas products. Further studies on the mechanism of glucose deposition were conducted by the same authors [10], in which erythrose was the main product and its potential forming pathway suggested that glucose was first isomerized by ring opening, and then erythrose was generated through reverse aldol condensation reaction. Unlike conventional cellulose pyrolytic processes, the proportions of fructose, erythrose, and glyceraldehyde were higher than that of 1,6-anhydroglucose (LG) [11]. This reveals that there should be different routes existing to generate these products comparing with that in vacuum pyrolysis reactions. Sasaki et al. [12,13] investigated the influences of the temperature and pressure on the glucose conversion to glycolaldehyde, LG, and 5-HMF. They found that the major pathway of the glucose conversion was retro-aldol reaction under lower density condition and the dehydration process was enhanced in higher water density conditions, and the proportion of HAA can reach its peak at certain condition. Moreover, smaller cellulose model compound like glyceraldehyde was also selected and investigated on its chemical performance under SCWC to unveil the mechanism of conversion in cellulose [14]. Whereas, the mechanism of glucose conversion under SCWC remains unclear. Hence, it is of importance to explore the intrinsic chemical reactions and to uncover the mechanism of product formation. This could shed some light on the mechanisms of the whole cellulose decomposition under similar conditions.

Density functional theory (DFT) has been extensively used to study the chemical reactions in organic structure and has illuminated some phenomenon in certain experiments theoretically [15–17]. Numbers of relative calculations have been reported to elucidate the catalytic role of water molecule, which was regarded as having the pivotal role in glucose and cellulose chemical conversion reactions under SCWC. In the work conducted by Akiya and Savage [18], the activation barrier of formic acid decomposition may reduce in the transition state complex due to the presence of water. They also suggested that the water molecules act as a homogeneous catalyst for both dehydration and decarboxylation. Furthermore, Takahashi et al. [19], conducted ethanol oxidation into acetaldehyde employing *ab initio* calculation to reveal the catalytic role of water in supercritical conditions. They found that the direct participation of water molecules through a multi-center transition state including an ethanol molecule and two water molecules bridging the oxygen atom of ethanol and the α -hydrogen

substantially reduced activation energy of the oxidation compared to those in the absence of water molecules. A similar chemical reaction process was observed in glyceraldehyde [20], which was a simplified glucose model compound that can be converted into pyruvaldehyde and glycolaldehyde by dehydration and retro-aldol reaction [21], respectively. The DFT calculation results indicated that the presence of water on the dehydration and the tautomerism reaction reduced the activation energy barriers, and dehydration was consistently more favorable than tautomerism and retro-aldol reaction. It was postulated that the water molecules directly participated in the transition state to form the ring-like water bridge [20]. Nevertheless, glyceraldehyde is only one kind of product generated from glucose, and cannot represent the whole chemical reaction characters of glucose. Therefore, it is important to study the glucose and cellulose conversion processes to uncover the mechanism of chemical reactions, especially exploring the effects of water molecules in supercritical water. In the present work, density functional theory (DFT) calculations of beta-D-glucose conversion were performed to elucidate the reaction mechanisms in terms of effects of water molecule on the dehydration and products formation reactions under SCWC.

2. Computational details

2.1. Design of reaction pathways

The beta-D-glucose decompositions through dehydration, retro-aldol reaction and tautomerization were investigated and the main products, such as glycolaldehyde, erythrose, glyceraldehyde, fructose, 5-hydroxymethylfurfural, levoglucosan, were generated in different reaction pathways. Eight systematic dehydrations (H1~H8) occurred between two adjacent carbon atoms in beta-D-glucose. Specifically, the hydroxyl on C1 can be removed along with the hydrogen on C2 (H1). The hydroxyl on C2 can be removed by two ways – with hydrogen on C3 (H2) or with the hydrogen on C1 (H3). The hydroxyl on C3 can be removed through two ways – with H on C4 (H4) or on C2 (H5). Similarly, the hydroxyl on C4 can be removed with H on C5 (H6) or C3 (H7), and finally, the C6 hydroxyl can be removed with H on C5 (H8). Apart from direct hydration reactions, ring-opening reaction was the most important reaction, after which most outcomes could be formed, such as, Glycolaldehyde, erythrose, glyceraldehyde, fructose, 5-hydroxymethylfurfural were generated through dehydration reaction, retro-aldol reactions keto-enol tautomerization and structure rearrangement after beta-D-glucose ring opens, which was shown in Fig. 1.

2.2. Computation method

The density functional theory (DFT) method based on quantum mechanics was employed in the present study. Under the supercritical water condition (673 K and 25 MPa), the equilibrium geometries of all reactants, intermediates, transition states and products involved in every chemical reaction were performed at B3LYP method [22] with AUG-cc-pVDZ basis set [23–26], which is a more accurate basis set than that used in our previous work. In order to simulate the water surrounding, the water solvent effect was considered in every chemical reactions with or without water molecule assistance by using the classic water solvent model, which is embedded in Gaussian software and has been applied successfully in previous relevant study [27]. The transition states were located by the synchronous transit-guided quasi-Newton method according to the structures of reactants and products and were confirmed by frequency analysis and intrinsic reaction coordinate (IRC) calculations with the same basis set. All energies of structures were

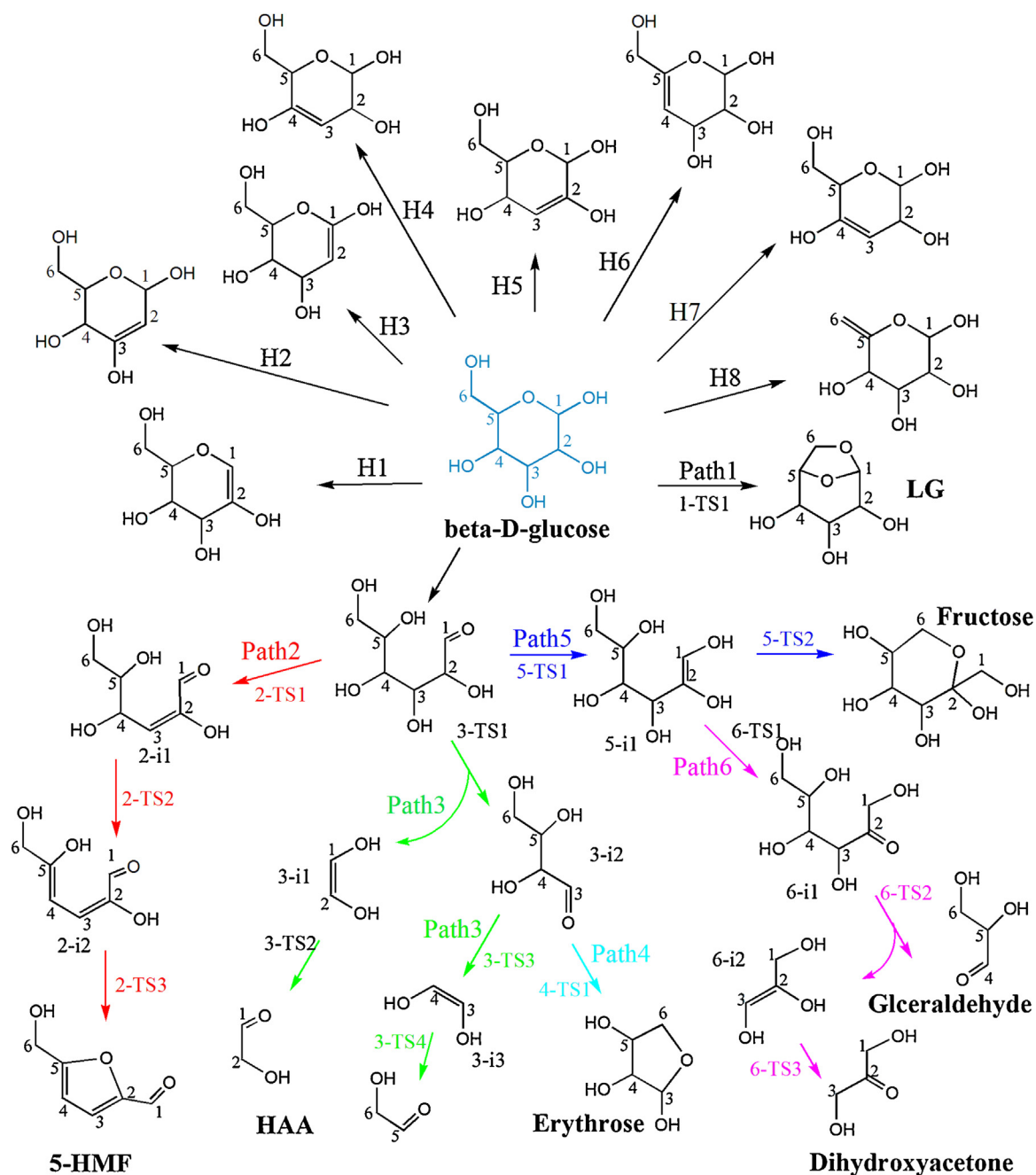


Fig. 1. Beta-D-glucose conversion pathways considered in this study.

obtained after zero-point energy (ZPE) correction. The correctness of all the optimized structures were confirmed through frequency analysis in which reactants, intermediates and products had no imaginary frequencies while transition states had exactly one imaginary frequencies. All calculations were performed by employing Gaussian 09W suite of programs [28], with key words of “temperature = 673 and pressure = 25” and “scrf = (solvent = water)”.

3. Results and discussions

3.1. Beta-D-glucose hydration with and without catalytic water molecule

The beta-D-glucose inner-molecule dehydration reactions can occur in eight different ways (H1 ~ H8), in which the H atom and

–OH group on adjacent carbon atoms are removed to form one water molecule. Fig. 2 shows the optimized structures of reactants and eight transition states in different dehydration reactions. And Cartesian coordinates of all structures were list in Table 1 in Supporting information. All the reactants in different reactions were the same structure (R), due to that no significant energy differences were found against the case of beta-D-glucose as the reactant structure according to our previous work [16]. Thus, the same compound of reactant was adopted as a departure structure on the dehydration reactions in the absence of catalytic water molecule. It can be clearly seen that all the transition states (labeled from H1-TS to H8-TS) are the structures that have a four-atoms ring, two of which are H and O atom following being to the water molecule and the rest are two carbon atoms following with transferring from C–C bond to C=C bond within the ring. Among these four atoms directly reacting

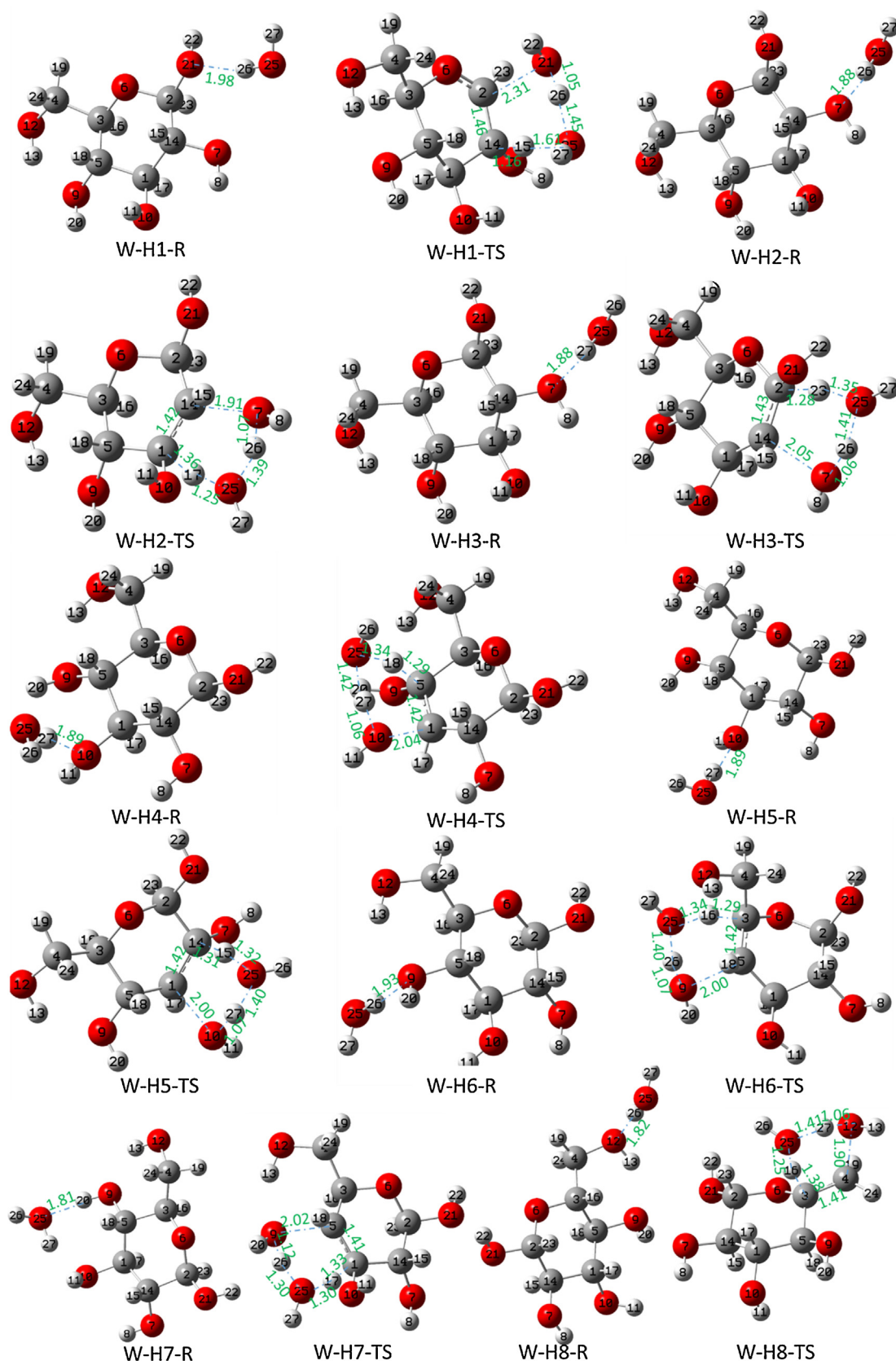


Fig. 3. Structures of reactant(R) and transition states on hydration reactions with water molecule.

attaches to beta-D-glucose and forms the intermolecular hydrogen bond against the hydroxyl group which will take part in the following dehydration reaction. In the transition states, one hydrogen

atom in the water molecule migrates to the hydroxyl group connected with the carbon atom to generate a new water molecule and the H atom transfers from carbon atom to the O atom of water

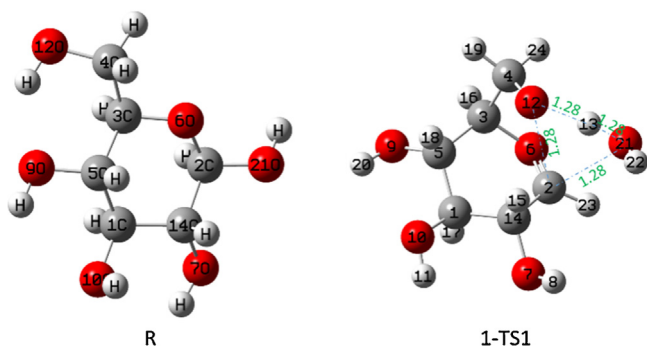


Fig. 4. Structures of reactant(R) and transition states on forming LG.

molecule at the same time, result in the atoms related to the reaction to form a six-atom ring. All the energy barriers of dehydration with water molecule catalyst are also listed in the Tab 1. In compare with energy barriers without water molecule, adding water molecule can reduce the energy barrier on the transition states with around 50 kJ/mol, which may be due to that the water molecule stimulates hydrogen atom transfer in dehydration reaction.

3.2. Beta-D-glucose conversion to products with and without catalytic water molecule

3.2.1. Reaction pathway 1~4

Levoglucosan is an important outcome in the process of cellulose pyrolysis [32], and its forming route was proposed that the concerted reaction pathway is the most rational mechanism. In the

transition state converting from glucose to LG [16], the dehydration occurs between -O6H and -O1H hydroxyl groups and generates a seven-atom ring: C1-O5-C5-C6-O6-H-O1 in 1-TS1, which is shown as 2C-O5-3C-4C-12O-13H-21O in Fig. 4. It is also the way which leads to cellulose chain decomposition under traditional pyrolytic condition. In order to investigate the effect of supercritical water on this process, the reaction was studied under SCWC. The energy barrier of this step is 218 kJ/mol, which is close to 207 kJ/mol under pure pyrolytic condition [31]. Unlike former dehydration reactions, the effect of water molecule on transition state to generate LG was not found according to several theoretic calculations. Therefore, the catalytic water has little influence on forming LG via concerted mechanism.

Ring-opening reaction is one of the key chemical steps in beta-D-glucose decomposition. Fig. 5 shows that in the transition state of 2-TS the H atom transfers from -O1H (signed with 21 O-H) to O5 (signed with 6O) to form a new hydroxyl group -O5H with the C1-O5 bond breaking and resulting in the generating of intermediate structure 2-i1. In the pathway 2, three continuous dehydration reactions take place to from the 5-HMF. Table 2 lists energy barriers of these four chemical processes, and it can be seen clearly that the last dehydration is the rate-controlled step because of its highest energy barrier in 2-TS3. The result is similar to that of under pure pyrolytic condition [31], which also indicates that there are little influence on the 5-HMF producing from glucose without water molecule. Similar to the former dehydration reactions discussed, water molecule should have pivotal influence in dehydration processes in pathway 2. Fig. 6 describes some main structures in pathway 2 with water catalyst. Interestingly, water molecule also acts as the catalyst on ring-opening step. In the tran-

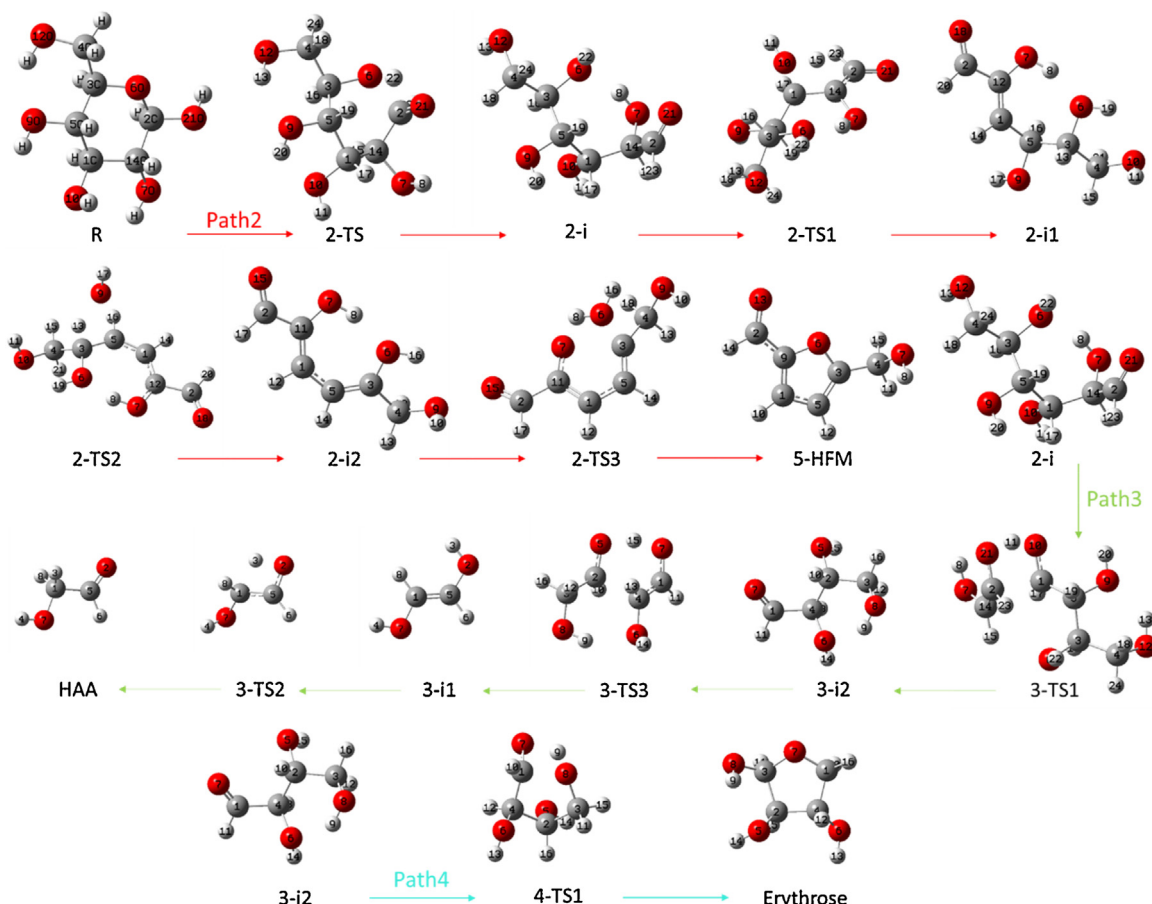
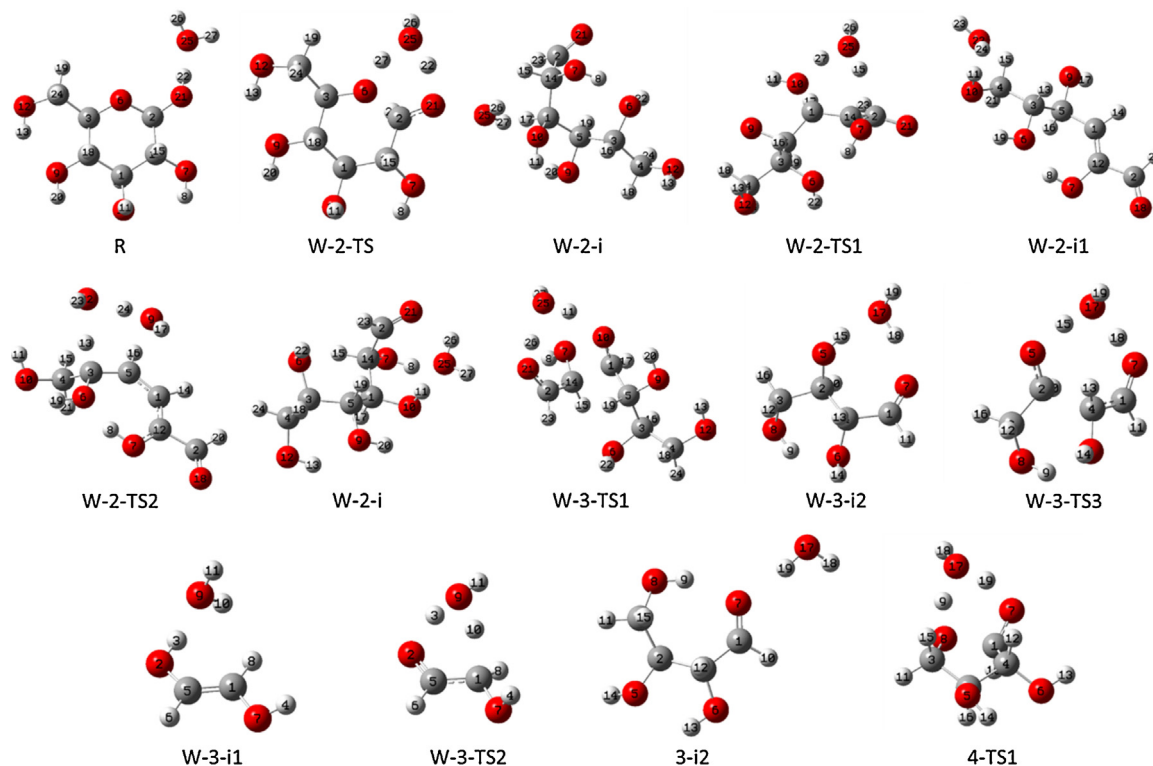


Fig. 5. Structures of pathway 2–4 without water catalyst.

Table 2

Energy barrier of each reaction transition state in pathway 2 (kJ/mol).

	2-TS/W2-TS	2-TS1/W-2-TS1	2-TS1/W-2-TS1	2-TS1/W-2-TS1
Without H ₂ O	176	194	225	260
With H ₂ O	93	152	188	/

**Fig. 6.** Main structures in pathway 2–4 with water catalyst.

sition state W-2-TS, a six-atom ring (6O-27H-25O-22H-21O-2C) is formed because 22H leaves from 21O to 25O in water molecule and 27H departs from water molecule to 6O in the glucose. This specific transition state structure effectively lowers the energy barrier from 176 to 93 kJ/mol, which is shown in Table 2. The energy barriers in following two dehydrations also drops dramatically. Whereas, the transition state in the third dehydration between two hydroxyl groups was not found. So it can be indicated that water molecule cannot act as the catalyst in this rate-control reaction in pathway 2 like that of forming LG. Therefore, it still needs to conquer a high energy barrier 260 kJ/mol to form 5-HMF in SCWC. This is in accordance with small proportion of 5-HMF in relative experimental results [12,33,34].

HAA is an important small molecule weight product during vacuum pyrolysis of cellulose [35] and recent experimental results indicated that HAA takes the largest proportion of cellulose hydrolysis under SCWC [34]. Three HAA molecules are generated in pathway 3 via retro-aldol reactions and tautomerization described in Fig. 1. The main structures in this pathway are listed in Fig. 5. Intermediate compounds 3-i1 and 3-i2 are generated from 2-I through transition state 3-TS1, in which 11H transfers from 10O to 21O and the 1C-14C bond breaks at the same time. The 3-i2 can further react through retro-aldol reaction to form HAA and 3-i3, then the structure 3-i1 and 3-i3 undergoes tautomerization to generate HAA. In the pathway 4, 3-i2 can react through 4-TS1 to form erythrose, in which 9H transfers from 8O to 7O and the 8O gets close to 1C to generate new -7O9H hydroxyl group and 1C-8O bond, respectively. All the energy barriers in these reactions without water catalyst are listed in Table 3. It shows that the rate-

control step in pathway 3 are 3-i1 and 3-i4 tautomerizations (3-TS2 and 3-TS4) which have an energy barrier of 229 kJ/mol. On the contrary, the retro-aldol reaction has a lower energy barrier. A different situation will occur when the water reacts in the chemical processes as described in Fig. 6. In the transition state W-3-TS1, 11H departs from 10O to 25O in the water molecule and 26H transfers from water molecule to 21O, also the 14C-1C single bond breaks and a new 2C=14C double bond is coming to being at the same time. A similar catalytic step happens in W-3-TS3. Surprisingly, the water catalyst has a negative effect on these retro-aldol reactions, in which the energy barrier with water is slight higher than that of without it. This result is different from that in the literature [27]. It is indicated that some difference exists in effects on retro-aldol reactions when different compounds are employed. On the other hand, it has a positive effect on tautomerizations of 3-i1 and 3-i3 when water catalyst is added. Moreover, the energy barrier of W-4-TS1 drops dramatically with water catalyst from 137 kJ/mol to 59 kJ/mol. When taking the whole reaction pathway into consideration, the energy barriers of forming both HAA and erythrose decrease to 128 kJ/mol with water assistance.

Fructose, glyceraldehyde and dihydroxyacetone are generated through pathway 5 and 6. In Fig. 7, the intermediate compound 2-i can react to 5-i1 via 5-TS1, in which 15H transfers from 14C to 21O to form a new hydroxyl group and the 2C=14C bond with energy barrier of 284 kJ/mol. Then the -12O13H group attaches to 2C=14C bond to form a four-atom ring through 5-TS2, result in a new outcome of fructose with the energy barrier of 193 kJ/mol in pathway 5. Energy barriers of these two reactions decrease to 163 and 142 kJ/mol in W-5-TS1 and W-5-TS2 with water catalyst,

Table 3
Energy barrier of each reaction transition state in pathway 3 and 4 (kJ/mol).

	3-TS1/W-3-TS1	3-TS2/W-3-TS2	3-TS3/W-3-TS3	4-TS1/W-4-TS1
Without H ₂ O	118	229	110	137
With H ₂ O	128	116	117	59

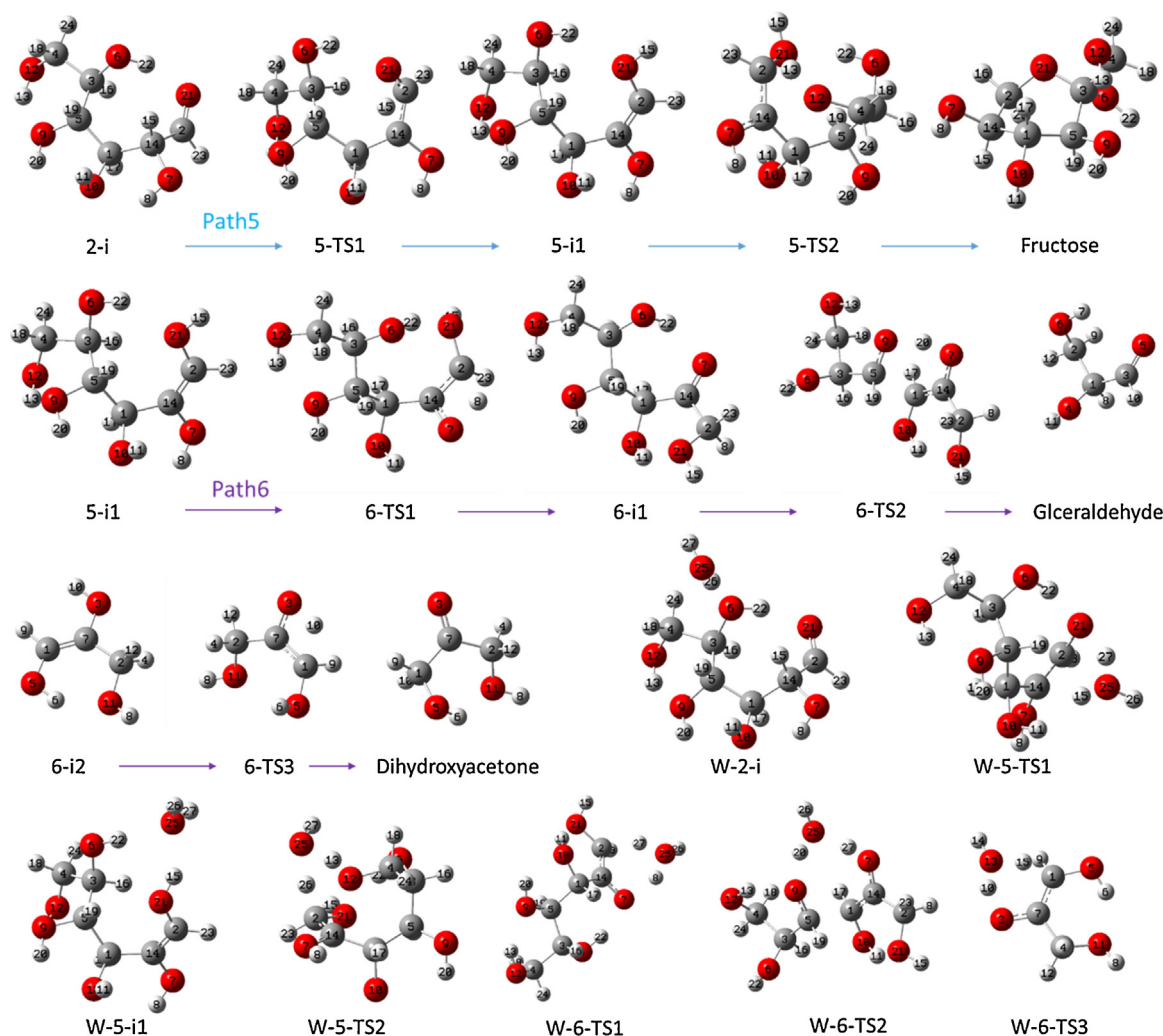


Fig. 7. Main structures of pathway 5–6 with and without water catalyst.

Table 4
Energy barrier of each reaction transition state in pathway 5 and 6 (kJ/mol).

	5-TS1/W-5-TS1	6-TS1/W-6-TS1	6-TS2/W-6-TS2	6-TS3/W-6-TS3
Without H ₂ O	284	203	118	221
With H ₂ O	163	86	119	106

respectively, which are shown in Fig. 7. In the pathway 6, the intermediate structure 6-i1 is generated from 5-i1 via 6-TS1 which is a tautomerization reaction between C=C and hydroxyl group with the energy barrier of 203 kJ/mol. Then glyceraldehyde and 6-i2 are generated by retro-aldol reactions through 6-TS2 with energy barrier of 119 kJ/mol. Dihydroxyacetone was produced from 6-i2 via tautomerization with energy barrier of 221 kJ/mol. It can be seen from Table 4 that the rate-control step in pathway 6 is located in 5-TS1, which energy barrier is 284 kJ/mol. A much lower energy barrier was obtained with the assistance of water molecular and therefore the products of glyceraldehyde and dihydroxyacetone are enhanced by water catalyst.

According to former discussion, it can be concluded that a sharp decrease exists in energy barrier of generating these main products except for 5-HMF with the catalyst of water molecule. Compared with other outcomes studied, the energy barrier of forming 5-HMF is the largest one (260 kJ/mol), which is the reason why it has the smallest proportion during beta-D-glucose conversion under SCWC [33,34]. On the contrary, both forming HAA and erythrose have the lowest energy barrier of 128 kJ/mol. But the proportion of HAA was larger than that of erythrose due to that in the pathway 4 one HAA molecule will be produced along with forming one erythrose molecule. These results rationally interpret high yield of HAA and erythrose in relevant experiments [7,12,33,34]. Moreover, the

formation of fructose, glyceraldehyde and dihydroxyacetone also have a low energy barrier of 163 kJ/mol, which makes it possible for them to be main outcomes in this chemical processes [5,10]. Adding water catalyst could lower the energy barrier of dehydration. Whereas, a slight negative influence occurred in retro-aldol reactions caused by water molecule [12]. Even so, the energy barrier of retro-aldol reaction is lower than that of dehydration. Therefore, it makes sense that retro-aldol reactions are major route of the glucose conversion under lower density water conditions and the dehydration is enhanced in higher water density conditions [36,37]. Moreover, the direct dehydration reaction in glucose has the highest energy barrier than any other reactions. But the dehydration after ring-opening reaction has a relative low energy barrier, which indicates that the dehydration prefer to occur after fragmentation reaction. This result is in accordance with phenomenon in the experiment [36].

4. Conclusion

In order to better understand the mechanism of cellulose decomposition under SCWC, DFT calculations of beta-D-glucose conversion were performed in terms of the presence or the absence of catalytic water molecule. Eight dehydration reactions and 6 reaction pathways forming main products were studied. The calculation results indicate that the dehydration in glucose needs high energy barriers, which is less favorable to take place during glucose conversion. While the water molecule can act as a homogeneous catalyst in the dehydration reaction by forming six-atom rings in the transition states, which can reduce the energy barriers of all dehydrations including dehydration reactions taking place after ring-opening. Meanwhile, the water molecules also have pivotal role in the pathways forming main outcomes, which also lower the energy barriers of keto-enol tautomerization and structure rearrangement. With the assistance of water molecule the generation of HAA and erythrose in pathways 3 and 4 both have the lowest energy barrier of 128 kJ/mol, which is consistent with the highest proportion of yield of productions in relative experiments. A somewhat higher energy barrier (163 kJ/mol) is needed to form glyceraldehyde and fructose in pathways 5 and 6, which echo with their being of the main products. However the energy barriers of forming LG and 5-HMF are 218 and 260 kJ/mol in pathways 1 and 2, respectively. Because of their comparative high energy barrier, it is reasonable to illustrate their minor yield in the conversion products. Therefore, these reactions analysis in terms of water molecule participation can explain the mechanism of generating main outcomes from glucose and the catalyst role of water molecule in molecular level, which also highlights the step to explore the decomposition of cellulose in supercritical water.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 51576019) and Chongqing university postgraduates' innovation project (CYB15016). One of the authors, Yayun Zhang, would like to acknowledge financial support from the Chinese Scholarship Council (CSC).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jaap.2016.02.018>.

Reference:

- [1] M. Parikka, Biomass Bioenergy 27 (2004) 613.
- [2] M.J. Antal, S.G. Allen, D. Schulman, X. Xu, R.J. Divilio, Ind. Eng. Chem. Res. 39 (2000) 4040.
- [3] Y. Lu, L. Guo, C. Ji, X. Zhang, X. Hao, Q. Yan, Int. J. Hydrogen Energy 31 (2006) 822.
- [4] P.T. Williams, J. Onwudili, Ind. Eng. Chem. Res. 44 (2005) 8739.
- [5] B.M. Kabyemela, T. Adschiri, R.M. Malaluan, K. Arai, Ind. Eng. Chem. Res. 36 (1997) 1552.
- [6] M. Sasaki, Z. Fang, Y. Fukushima, T. Adschiri, K. Arai, Ind. Eng. Chem. Res. 39 (2000) 2883.
- [7] M. Sasaki, T. Adschiri, K. Arai, AIChE J. 50 (2004) 192.
- [8] S. Saka, T. Ueno, Cellulose 6 (1999) 177.
- [9] D. Yu, M. Aihara, M.J. Antal Jr., Energy Fuels 7 (1993) 574.
- [10] B.M. Kabyemela, T. Adschiri, R.M. Malaluan, H. Ohzeki, Ind. Eng. Chem. Res. 36 (1997) 5063.
- [11] K. Ehara, S. Saka, J. Wood Sci. 51 (2005) 148.
- [12] M. Sasaki, K. Goto, K. Tajima, T. Adschiri, K. Arai, Green Chem. 4 (2002) 285.
- [13] M. Sasaki, M. Furukawa, K. Minami, T. Adschiri, K. Arai, Ind. Eng. Chem. Res. 41 (2002) 6642.
- [14] B.M. Kabyemela, T. Adschiri, R. Malaluan, K. Arai, Ind. Eng. Chem. Res. 36 (1997) 2025.
- [15] S. Wang, X. Guo, T. Liang, Y. Zhou, Z. Luo, Bioresour. Technol. 104 (2012) 722.
- [16] Y. Zhang, C. Liu, H. Xie, J. Anal. Appl. Pyrolysis 105 (2014) 23.
- [17] S.H. Mushrif, V. Vasudevan, C.B. Krishnamurthy, B. Venkatesh, Chem. Eng. Sci. 121 (2015) 217.
- [18] N. Akiya, P.E. Savage, AIChE J. 44 (1998) 405.
- [19] H. Takahashi, S. Hisaoka, T. Nitta, Chem. Phys. Lett. 363 (2002) 80.
- [20] T. Honma, M. Hakamada, Y. Sato, K. Tajima, H. Hattori, H. Inomata, Density functional theory study of glyceraldehyde hydrolysis in supercritical water, The 2006 Annual Meeting (2006).
- [21] Z. Srokol, A.-G. Bouche, R.C. van Estrik, T. Maschmeyer, J.A. Peters, Carbohydr. Res. 339 (2004) 1717.
- [22] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
- [23] D.E. Woon, T.H. Dunning Jr., J. Chem. Phys. 98 (1993) 1358.
- [24] R.A. Kendall, T.H. Dunning Jr., R.J. Harrison, J. Chem. Phys. 96 (1992) 6796.
- [25] T.H. Dunning Jr., J. Chem. Phys. 90 (1989) 1007.
- [26] K.A. Peterson, D.E. Woon, T.H. Dunning Jr., J. Chem. Phys. 100 (1994) 7410.
- [27] T. Honma, H. Inomata, J. Supercrit. Fluids 90 (2014) 1.
- [28] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, 2013.
- [29] X. Zhang, W. Yang, W. Blasziak, J. Anal. Appl. Pyrolysis 96 (2012) 110.
- [30] M. Zhang, Z. Geng, Y. Yu, Energy Fuels 25 (2011) 2664.
- [31] Y. Zhang, C. Liu, J. Anal. Appl. Pyrolysis 110 (2014) 297.
- [32] A.G.W. Bradbury, Y. Sakai, F. Shafizadeh, J. Appl. Polym. Sci. 23 (1979) 3271.
- [33] D.A. Cantero, M. Dolores Bermejo, M. Jose Cocero, Chemsuschem 8 (2015) 1026.
- [34] D.A. Cantero, C. Martinez, M.D. Bermejo, M.J. Cocero, Green Chem. 17 (2015) 610.
- [35] G.N. Richards, J. Anal. Appl. Pyrolysis 10 (1987) 251.
- [36] X. Lü, S. Saka, J. Supercrit. Fluids 61 (2012) 146.
- [37] M. Sasaki, K. Goto, K. Tajima, T. Adschiri, K. Arai, Green Chem. 4 (2002) 285.