ENDERGONSKI AUTOKATALITIČKI CIKLUS FRUKTOZE U EFIKASNOJ PROIZVODNJI 5-HIDROKSIMETILFURFURALA (5-HMF) IZ SPORE PIROLIZE MEZOKARPA GOJI BOBICA (GBM)

FRUCTOSE ENDERGONIC AUTOCATALYTIC CYCLE IN EFFICIENT PRODUCTION OF 5-HYDROXYMETHYLFURFURAL (5-HMF) FROM SLOW PYROLYSIS OF GOJI BERRY MESOCARP (GBM)

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Овај рад разматра могућу употребу отпада на бази воћа (Гоји бобица месокарпа (ГБМ)) за производњу кључних платформских хемикалија (5-хидроксиметилфурфурала (5-ХМФ)) кроз термо хемијску конверзију путем споре пиролизе, која је изведена коришћењем симултане термичке анализе (СТА). Оригиналност и значај овог истраживања огледа се у новим спознајама о улози молекула фруктозе у производњи 5-хидроксиметилфурфурала (5-ХМФ) кроз структурне карактеристике, манифестујући реципрочно понашање катализе у путу ендергонске реакције, дајући производе високе енергије. На основу предложених експерименталних и теоретских мрежа, нежељени споредни производи су потпуно блокирани, при чему утврђени резултати у овом истраживању јасно показују предност и синергистичког рада молекула супстрата (глукозе) и псеудо катализатора (фруктозе) за ефикасну производњу 5-ХМФ. Циклус фруктозе који се само поправља (изомеризација) кроз организацију „отворене" до „затворене" структуре објашњен је као кључни фактор, који је био одговоран за ефикасну аутокаталитичку линију фруктозе до жељеног производа, тумачећи високе приносе 5-ХМФ-а.

Кључне речи: *Отпад на бази воћа; Пиролиза; Аутокатализа; 5-ХМФ; Ендергонски циклус*

This paper considers possible uses of fruit-based waste (Goji berry mesocarp (GBM)) for the production of key platform chemicals (5-hydroxymethylfurfural (5-HMF)) through thermochemical conversion via slow pyrolysis, which was performed using simultaneous thermal analysis (STA). Originality and significance of this research is reflected in novel insights of fructose molecule role in the production of 5-hydroxymethylfurfural (5-HMF) through structural characteristics, manifesting reciprocal catalysis behaviour in an endergonic reaction pathway, giving high energy products. Based on proposed experimental and theoretical networks, the unwanted side products are totally blocked, where established results in this research clearly show advantages of synergistic work of the substrate molecule (glucose) and pseudo-catalyst (fructose) for the effective production of 5-HMF. The fructose self-repaired (isomerization) cycle through 'open' to 'closed' structure organization was explained as the key factor, which was responsible for the fructose effective autocatalytic lineage to the desired product, interpreting high yields of 5-HMF.

Keywords: *Fruit-based waste; Pyrolysis; Autocatalysis; 5-HMF; Endergonic cycle*

1. Introduction

Of all the forms of renewable energy sources, biomass is expected to play a very important role in the growing energy needs of the world in the coming period. That is because of the fact that only biomass from all renewable sources can be used to obtain liquid fuels comparable to existing fossil fuels, for which there is a huge demand in the world primarily for needs traffic. Namely, the consumption of liquid fuels dominates in relation to other energy carriers, and it is expected to re-

main so after 2030 [1]. Term "biomass" can be defined in different ways. In the broadest sense, biomass is the matter of biological origin or organic matter (composed of carbon compounds), which can be used on various ways and translate into different forms of energy (thermal, mechanical or electrical), gaseous, liquid or solid fuels (and/or in so-called "green" chemicals or biochemicals) [2]. Biomass as a raw material for biofuel production can be divided into: a) rich in starch, b) sugar (for example, sucrose, which belongs to oligosaccharides - carbon hydrates composed of 2 - 10 molecules of simple sugars), c) lignocellulosic biomass (dominated by cellulose and hemicellulose - structural polysaccharides in plants, accompanied by lignin - a macromolecular compound composed of phenylpropane units) and d) biomass rich in tropidol glycerol with higher fatty acids. The energy content of these basic biomass compounds, important from the point of view of its conversion into biofuels is different, and increases with an decreasing of the oxygen content and increasing hydrogen-carbon ratios in their molecules, so that energy content per unit mass decreases from lipids to lignins up to sugar, which have the lowest energy content [1]. In this context, the exploitation of biomass as renewable source of chemicals is an attractive possibility, in particular the one derived from food waste (FW).European Industrial Bioenergy Initiative (EIBI) was launched in November 2010 as a continuation of the proposals of the European Biofuels Technology Platform (EBTP) and the European Commission (European Biofuels Technology Platform, Advanced Biofuels in Europe) [3], recognizes advanced biofuels as fuels produced from lignocellulosic raw materials or (industrial) waste, which have low CO_2 emissions or a significant reduction in greenhouse gases, and have zero or very small ILUC (Indirect Land Use Change). So having the facts presented above, forasmuch capital and operating costs, GHG (greenhouse gas) emissions, the consumption of process chemicals and carbon efficiency, thermochemical conversions, with an indication of the pyrolysis process, are more effective [4].Present study aims to deepen in understanding the pyrolysis mechanism through kinetics analysis elucidating main reaction pathways that leads to production of valuable chemicals from Goji berry mesocarp (GBM) as FW source. A significant goal of this research is the use of advanced kinetic modeling through application of inverse (model-free) and direct (model-based) kinetic problem's resolving in recognition of carbohydrate polymers fractionation. Identification of value-added chemicals and precursors to biofuels was established on the basis of kinetic data obtained from the use of state-of-the-art computational software, NETZSCH Kinetics Neo. For details, regarding applied methods, reader is referred to https://kinetics.netzsch.com, kinetics.neo@netzsch.com. Originality and significance of this research is reflected in novel insights of fructose molecule role in the production of 5-hydroxymethylfurfural (5-HMF) through structural characteristics, manifesting reciprocal catalysis behavior in endergonic reaction pathway, giving high energy products.

2. Materials and methods

2.1 Sample preparation and thermo-analytical measurements

Fresh Goji berries were provided by A&S UNION D.O.O. Goji farm located in the Subotica City (North-Backi county), in the Republic of Serbia. All harvested fruits (harvest was done in July 2019) were randomly collected in the orchard from different plants and analysed as air-dried. The collected berries (about 1.0 kg of fresh berries packed in a plastic sealed bag) were frozen in the refrigerator at -8.0°C before use. For experimental analyses, defrosting of a single bulked sample was performed naturally in the current sealed bag at room temperature. The passive drying of the sample was performed by lying of Goji berries out onto dry trays, and leaving them in a warm, airy place, away from the direct light until thoroughly dried. After drying, the separation of Goji berry mesocarp from other parts (seeds and exocarp) of dried fruit was performed mechanically, with increased care to avoid mesocarp damage. One part of dried berries was set aside for mesocarp preparation in thermal analysis (TA) measurements. For the mechanical separation of fruit parts, the singled scalpel-knife was used for the mesocarp secluding without the exocarp.

The effect of pyrolysis process under an inert atmosphere was investigated by simultaneous thermogravimetry (TG) and derivative thermogravimetry (DTG) using NETZSCH STA 445 F5 Jupiter (Erich NETZSCH GmbH & Co. Holding KG, Germany) thermal analyzer equipment. The

purging gas was argon (Ar) (Class 5.0) with a flow rate of $\varphi = 40$ mL/min. The following heating rate values were used $\beta = 5.0, 10.0$ and 15.0 K/min. The heating rates were chosen to estimate the best conditions for performing a slow pyrolysis process. To reduce the influence of the sample quantity on the analyses, about $\Delta m = 5.10 \pm 0.01$ mg of the sample was used in a platinum pan for each measurement analysis. The mesocarp samples were submitted to a linear temperature gradient (programmed heating in a linear mode) ranging from room temperature (RT) up to 710 oC. TA device has user-friendly menus combined with automated routines within Proteus® software for processing thermo-analytical experimental data.

3. Results and discussion

3.1 TG – DTG measurements of Goji berry mesocarp (GBM) pyrolysis process

The mass loss (TG) and derivative mass loss (DTG) curves (as absolute mass loss rate curves) of the GBM feedstock sample in an argon (Ar) atmosphere at different heating rates ($\beta = 5.0, 10.0$ and 15.0 K/min) are presented in Fig. 1 a) – b). It can be observed from the mass loss – temperature (TG) features at all heating rates (Fig. 1 a)) that GBM feedstock retains a significant amount of water after air drying, where moisture removal intensifies to approximately 125°C (the reaction step 1). The mass loss of the sample in this stage gradually decreases with an increasing of heating rate. This drop of the sample mass is a consequence of the water loss during the temperature rise (parallel with raising the heating rate value). So, the first phase of the process can be attributed to the thermal dehydration of GBM feedstock, but it is possible to expect and decarboxylation process in the labile compounds. As shown in Fig. 1 b), the trend of DTG curves is affected by applied heating rate. In detail, it can change the temperature of the characteristic – peak (maximum) temperature and the curve shape. It should be noted that the rate effect on the thermo-analytical curves reflects that thermal events which occurs have kinetics origins, indicating the need for determination of kinetic parameters for the major events and thermal shift of events with a heating rate applied.
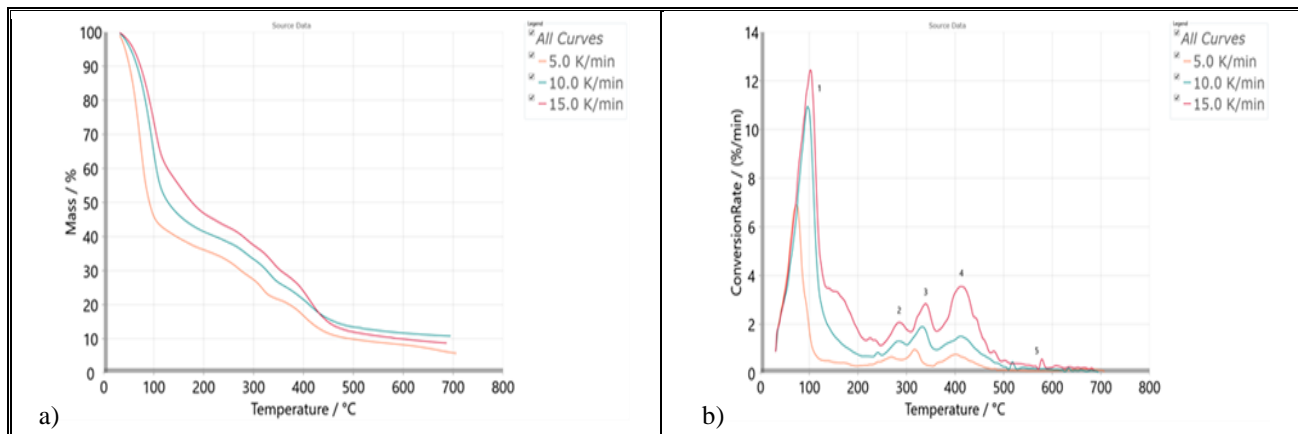

Figure 1. a) TG) curves, b) absolute DTG (conversion rate) curves of GBM pyrolysis at 5.0, 10.0 and 15.0 K/min (ordinal numbers "1 – 5" represent identified reaction stages) (images are directly imported from NETZSCH Kinetics Neo software)

Within the first reaction step (1), the water evaporation is more intensive, but applying highest heating rate, the broader "shoulder" appears on DTG curves at about 150°C (Fig. 1 b)). It seems that with an increasing of the heating rate, this step becomes more complex, where higher heating rate probably activates some of organic constituents in GBM, causing the significant bulk shrinkage of the sample. The main pyrolysis temperature intervals related to reaction steps 2, 3 and 4 which are clearly differentiated (Fig. 1 b)), can be attributed to decomposition of fibers, such as hemicelluloses (200 – 300°C) and cellulose (300 – 360 oC) (peaks '2' and '3' – the hollocellulose pyrolysis), and the decomposition of carbohydrates (sugars) with most prominent DTG peak (Fig. 1 b)) for 360°C – 475°C [5].Since, it has been reported that the lignin decomposition take place over a wide temperature interval [6], the main lignin pyrolysis probably occurs above 500°C (considering reac-

tion step 5). It should be emphasized that the biomass feedstock with the high volatile matter (VM) content may generates a lot of large molecular compounds, so that a more activation energy was needed to overcome the energy barrier and drive pyrolysis process further. Thus, at high temperatures, some of lipid molecules may evaporates and remote decomposition of them demanding more activation energy inputs. Therefore, these lipids can repair pyrolysis activation energy at the end of the entire process. In that manner, the model-free analysis is necessary to be performed in order to closely define multi-step nature of the current process, especially in the optimization of operating parameters.

3.2 Kinetic analysis

Based on the applied model-free kinetic methods (kinetics.neo@netzsch.com), it is possible to make a general prediction of some of possible reaction steps by presenting results through 3-D color trajectory contour of conversion (x) – temperature (T) – activation energy (Ea) profile as shown in Fig. 2.

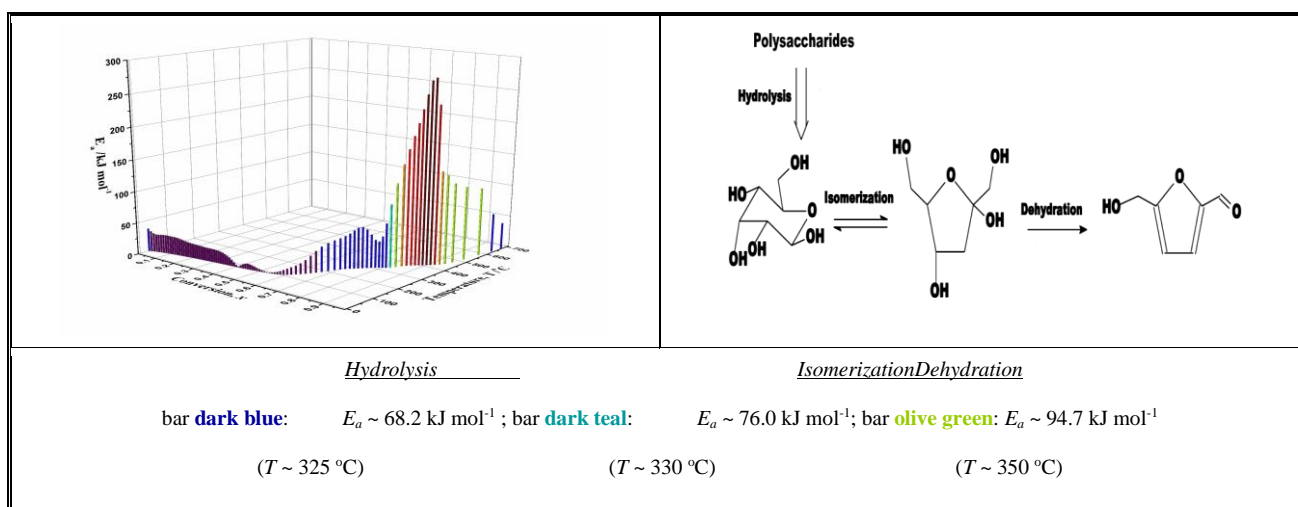| _Hydrolysis_	_IsomerizationDehydration_	
bar **dark blue**: $E_a \sim 68.2$ kJ mol^{-1} ; bar **dark teal**:	$E_a \sim 76.0$ kJ mol^{-1}; bar **olive green**: $E_a \sim 94.7$ kJ mol^{-1}	
($T \sim 325$ °C)	($T \sim 330$ °C)	($T \sim 350$ °C)

Figure 2. 3-D color trajectory contour of conversion (x) – temperature (T) – activation energy (Ea) values obtained by model-free kinetic approach of GBM slow pyrolysis and interpretation of model-based results in the high-temperature process region related to the products of cellulose (polysaccharide) decomposition, where one of important product of identified thermal transformation represents 5-hydroxymethylfurfural

One of the key reaction steps is the hydrolysis process of polysaccharides (cellulose molecule) to glucose (Fig. 2) which takes place via activation energy of Ea = 68.2 kJ mol-1 [7], and then subsequently isomerization of glucose to D-fructose (Fig. 2) occurring with a slightly higher Ea value (where for this reaction, the Ea values in the range of 35.0 – 75.0 kJ mol-1 were reported [8]) (Fig. 2). However, it was reported that the Ea value for isomerization of glucose may varies in a wider range, which strongly depends on the reaction environment, especially in the presence of catalyst type involved [9]. Furthermore, the production of key intermediate platform chemical such as 5-hydroxymethylfurfural (5-HMF) (which is shown in scheme in Fig. 2) from D-fructose dehydration proceeds via higher Ea value of 94.7 kJ mol-1, and it is obvious that current reaction takes place in a higher temperature region. From kinetics approach, the derived Ea value is in good agreement with a reported value in literature [10]. From model-based analysis (kinetics.neo@netzsch.com), for a temperature range of ΔT = 348.56 – 412.66 oC and conversion range of Δx = 0.83 – 0.90, autocatalytic rate curve for conversion of fructose to 5-HMF is constructed in a form of Vautocat5-HMF against time t (s), considering lowest heating rate. This plot is presented in Fig. 3 by square symbols. Kinetic data related to considered reaction step exhibit "S-shaped" behavior which obeys to expanded Prout-Tompkins (PT) autocatalytic kinetic model. This behavior can be qualitatively described with Logistic function of Verhulst type [11].
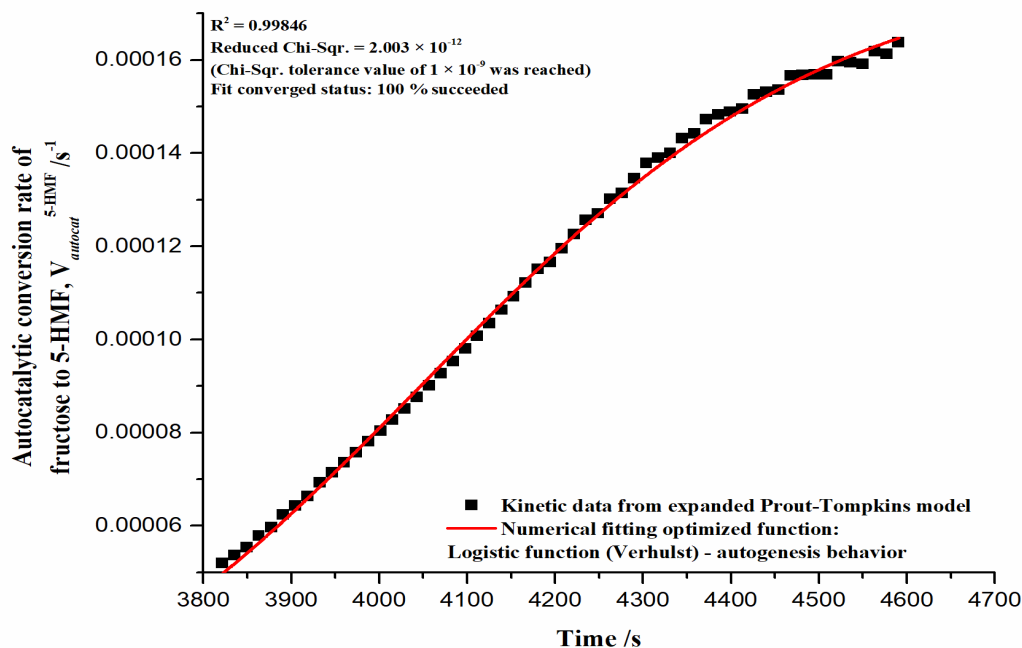
Figure 3. V_autocat^{5-HMF} vs. t plot formed on the basis of kinetic data from Prout-Tompkins model (isomerization step) in the temperature range between 348.56 °C and 412.66 °C (■ symbol). Data presented by full colored line (——) present the numerically fitted optimization function: Logistic function of Verhulst type, which manifests the autogenesis behavior (the same figure gives information regarding the statistical fitting parameters, such as R² and reduced Chi-Sqr. (χ²))

Given the established dependence in Fig. 3, characteristic addiction is reflected through non-linear amplification which is typical for self-organization. This tends to push thermodynamic conditions for further propagation toward unfavorable. In catalytic system, catalytic reaction rate can increase exponentially, as more and more catalysts are produced, up to the point when not enough reactants are available for further propagation and self-organizing process ends [12]. This mechanism works only when both viewpoints are taken into account, its *intrinsic* and *autocatalytic* side. Therefore, the autogenic reaction step under consideration consists of a mutually constraining coupling of intrinsic and autocatalytic decompositions, where limiting parameter represents the temperature (i.e., heating rate). Under the influence of temperature as regulatory factor in this catalytic system, the reaction initially leads to an increased probability for another reaction to take place as more and more catalysts are created. So, based on results obtained and their consequences, the considered stage of the process is reflected through the transformation which was shown in Figure 4.
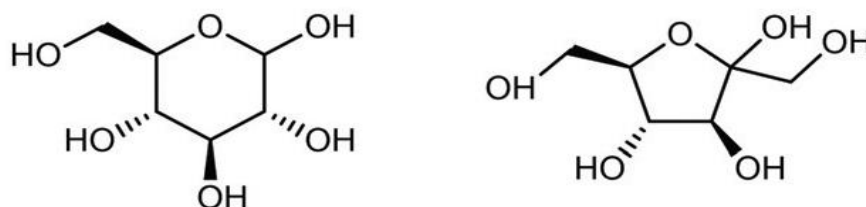
glucose Isomerization ('Lewis acid') *fructose*

*Figure 4. The intrinsic reaction step ('decomposition') described by isomerization **D**[glucose] ↔ **E**[fructose]*

The intrinsic step involves isomerization of glucose to fructose, where Lewis acids act as catalysts (such as Na^+, K^+ and Ca^{2+}) which are abundant in GBM. It was known that isomerization of glucose to fructose, catalyzed by a Lewis acid represents reversible reaction with a low yield and relatively low reaction efficiency, due to the constraint of the reaction equilibrium. However, in our case, based on above facts, the reaction equilibrium is severely disturbed. Namely, the described intrinsic kinetics of expanded PT model shows characteristics of autogen formation (AF). This means that **D ↔ E** (**Scheme 1**) is far from equilibrium, pushing the reaction balance towards the production of fructose in large quantities at relatively high temperatures. In that context, the entropy potential necessary for far from equilibrium system to become a self-organized, can be considered from the point of view of non-equilibrated chemical reaction. Therefore, non-equilibrium conditions imposed by external factors such as temperature represent the initial point before autocatalytic decomposition takes place. So by shifting the equilibrium towards creating fructose and since a much higher fructose yield is produced compared to the glucose yield (still present in the system), in a mixture, **E + D**, push reaction autocatalytically towards further increase in fructose yield. So, by input the thermal energy in the presence of "substrate" (glucose), and in the presence of two phases (these phases represents liquid (H_2O) and gaseous (CO_2 originated from decarboxylation) distinguished by their difference in chemistry and thermodynamic directionality, **E + D → 2E** forms autogenic work cycle (AWC). Latter can be explained as since that the catalysis lowers threshold that must be exceeded in order to initiate a chemical reaction, but once this threshold is crossed an energy gradient difference from the reactant to the product, it drives the reaction. Thus, the process is endergonic (endergonic = ingoing + work). By analogy of internal combustion engine, the energy that drives the autogenic cycle is provided by energy released by catalysis. This energy, liberated from chemical bonds of "substrate" molecules (glucose) is the *source* of the work which produces additional catalysts (in this case, fructose, which acts as pseudo-catalyst). Consequently, heat energy is absorbed, making fructose molecules to be in a higher energy state, apparently elevated the transition state energy barrier ($\Delta G^o > 0$ and $E_a\uparrow$ (**Fig. 2**)). Because of great accumulation of fructose (**2E**) (very high yield), fructose molecules are unstable which can promote opening a next decomposition pathway. Since at that moment, the fructose structure is far from equilibrium structure with a relatively high threshold required to dissipate it (in a form of serious structural/molecular changes), fructose is capable to easily capture the proton from surroundings, triggering dehydration in acidic environment. Besides autogen molecule (fructose) is not only able to self-repair (isomerization cycle), because of its cycling from 'open' to 'closed' structure organization, fructose strongly tends to acquire molecules from its surroundings. In this case, the captured chemical entity (H^+) which shares catalytic inter-reactivity with autogen catalyst (fructose) will tends to be incorporated in autogen catalyst, forming effective autocatalytic *lineage to the desired product, 5-hydroxymethylfurfural (5-HMF)*. So we can expect with high probability an abundant yield of 5-HMF. Considering these facts, they are in complete agreement with description of the process with expanded Prout-Tompkins model.

4. Conclusion

This work aimed to verify abilities of GBM to provide the production of value-added chemicals through slow pyrolysis process, performed by simultaneous TG-DTG measurements, under non-isothermal conditions. Development of pyrolysis mechanism which includes fragmentation of hollocellulose material to final products was followed by application of both, model-free (inverse) and model-based (direct) methods. It was established that intrinsic kinetics properties of fructose were described by expanded Prout-Tompkins (PT) model showing propriety of autogen formation (AF). It was concluded that fructose's autogenesis behavior provides limitation and preservation of some products (considering side reactions and formation of certain products).

Under dynamic conditions, fructose is capable for regeneration (self-repairing) through isomerization where its integrity is temporarily lost. Nevertheless, internally distributed confinements arranged in molecular structure, allow the energy to be recruited for 'substrate' (glucose) action to produce 5-HMF. This is strongly influenced by external regulatory factor, i.e. heating rate. There-

fore, heating rate magnitude affects the "organized work" of fructose, and thus maintaining its active capacity for transferability to glucose.

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