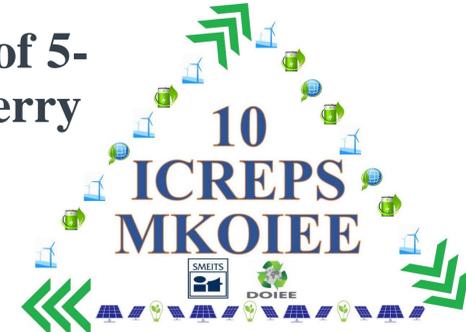# Fructose endergonic autocatalytic cycle in efficient production of 5-hydroxymethylfurfural (5-HMF) from slow pyrolysis of Goji berry mesocarp (GBM)Title

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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.
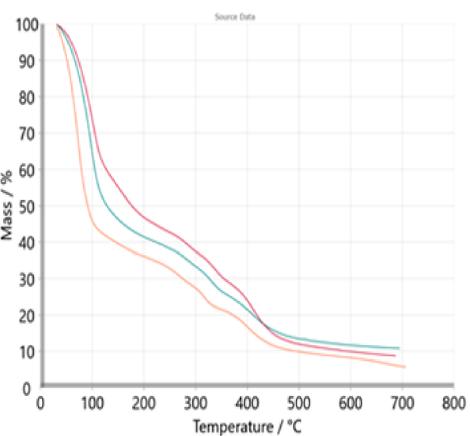
Results and discussion:

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 ºC) 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 ºC – 475 ºC [1].Since, it has been reported that the lignin decomposition take place over a wide temperature interval [2], the main lignin pyrolysis probably occurs above 500 ºC (considering reaction step 5).
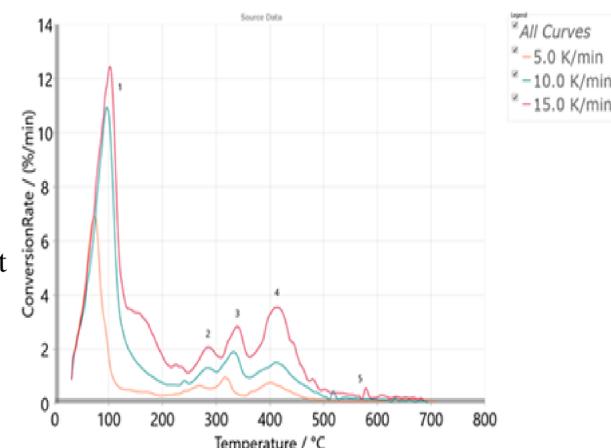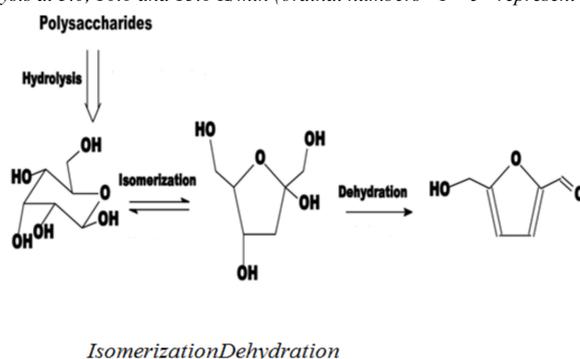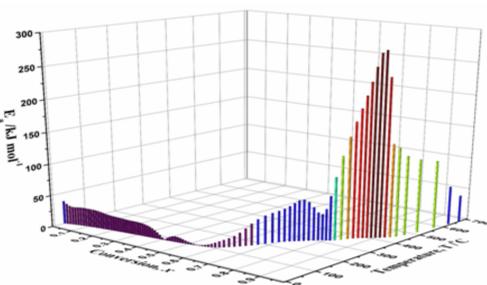

Fig. 1 a) TG) curves, b) absolute DTG (conversion rate) curves of GBM pyrolysis at 5.0, 10.0 and 15.0 K/min (ordinal numbers "1 – 5" represent identified reaction stages) (images are directly imported from NETZSCH Kinetics Neo software)

Hydrolysis
Isomerization   Dehydration

bar **dark blue**: $E_a \sim 68.2$ kJ mol^{-1} ; bar **dark teal**: $E_a \sim 76.0$ kJ mol^{-1}; **olive green**: $E_a \sim 94.7$ kJ mol^{-1}

($T \sim 325$ °C)   ($T \sim 330$ °C)   ($T \sim 350$ °C)

From model-based analysis, for a temperature range of $\Delta T = 348.56 – 412.66$ ºC and conversion range of $\Delta x = 0.83 – 0.90$, autocatalytic rate curve for conversion of fructose to 5-HMF is constructed in a form of $V_{autocat}^{5\text{-HMF}}$ 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 [3].

Fig. 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

Given the established dependence in **Fig. 3**, characteristic addiction is reflected through non-linear amplification which is typical for self-organization which tends to push thermodynamic conditions for further propagation toward unfavorable. In catalytic system, catalytic reaction rate can increases 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 [4].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.
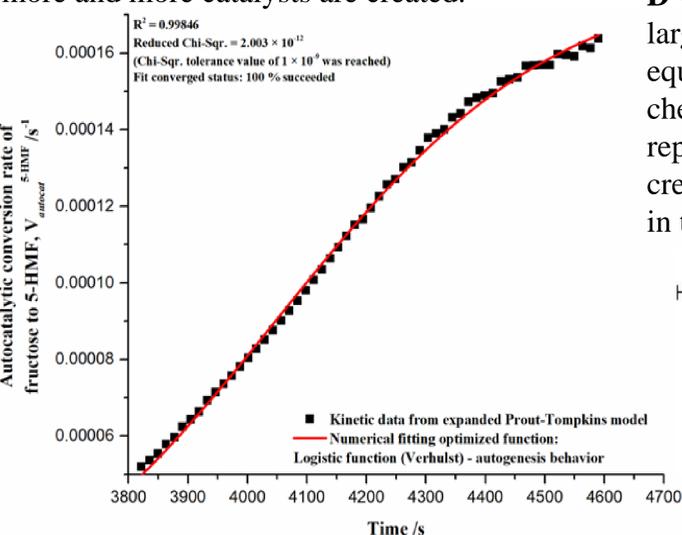

D ↔ E (**Scheme 1**) is far from equilibrium, pushing the reaction balance towards the production of fructose in large quantities at relatively high temperatures. In that context, the entropy potential necessary for far from equilibrium system to become a self-organized, can be considered from the point 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.

Scheme 1

glucose   isomerization ('Lewis acid')   fructose
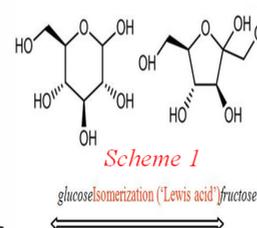
Consequently, heat energy is absorbed, making fructose molecules to be in a higher energy state, apparently elevated the transition state energy barrier ($\Delta G^o > 0$ and $E_a \uparrow$ (**Fig. 2**)). Because of great accumulation of fructose (**2E**) (very high yield), fructose molecules are unstable 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.

Fig. 3 $V_{autocat}^{5\text{-HMF}}$ vs. t plot formed on the basis of kinetic data from Prout-Tompkins model (isomerization step) in the temperature range between 348.56 ºC and 412.66 ºC (■ 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 R^2 and reduced Chi-Sqr. (χ^2))

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