MICROWAVE ASSISTED HYDROTHERMAL CARBONIZATION: A NEW OPTION TO OBTAIN CARBON NANOSTRUCTURES FROM BEET MOLASSES

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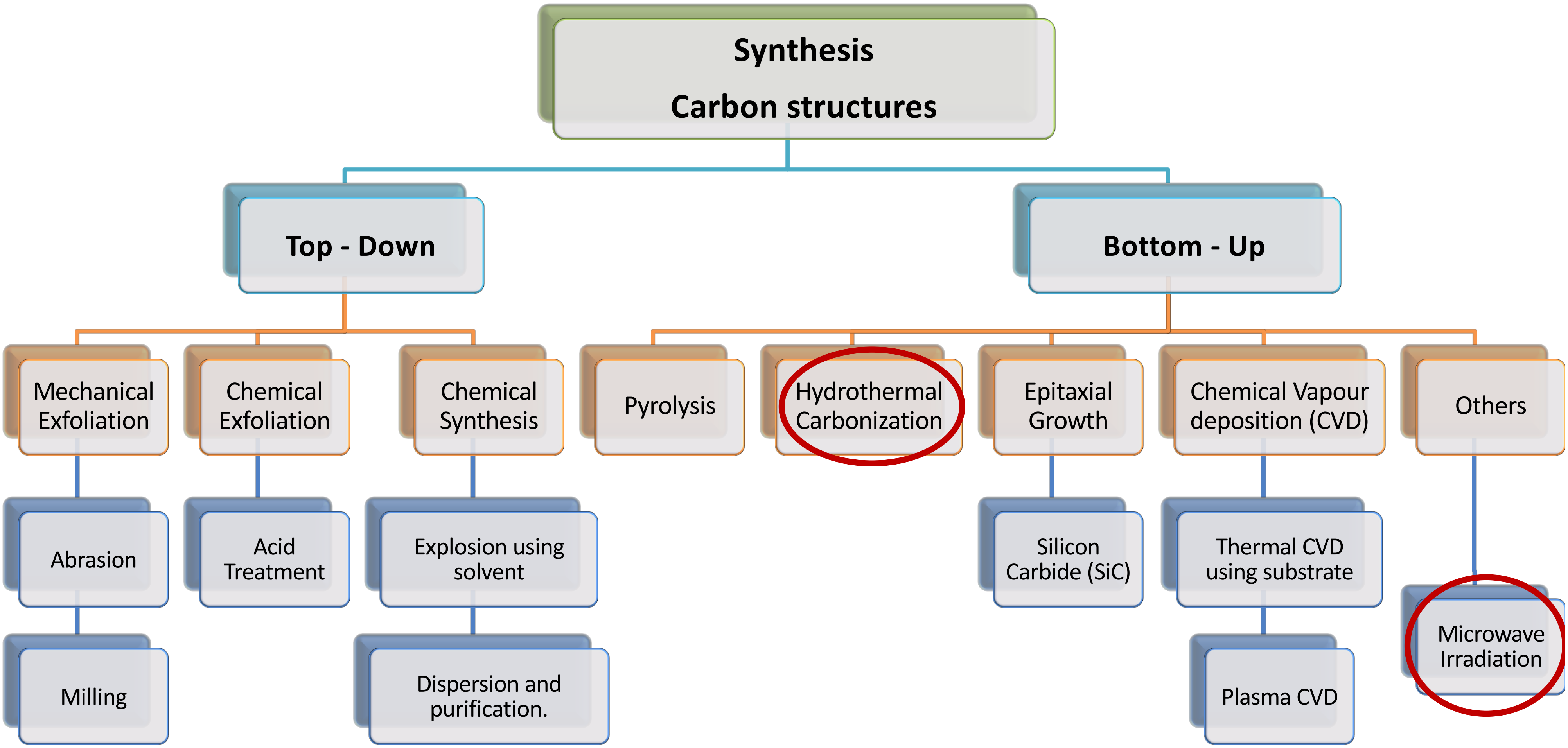
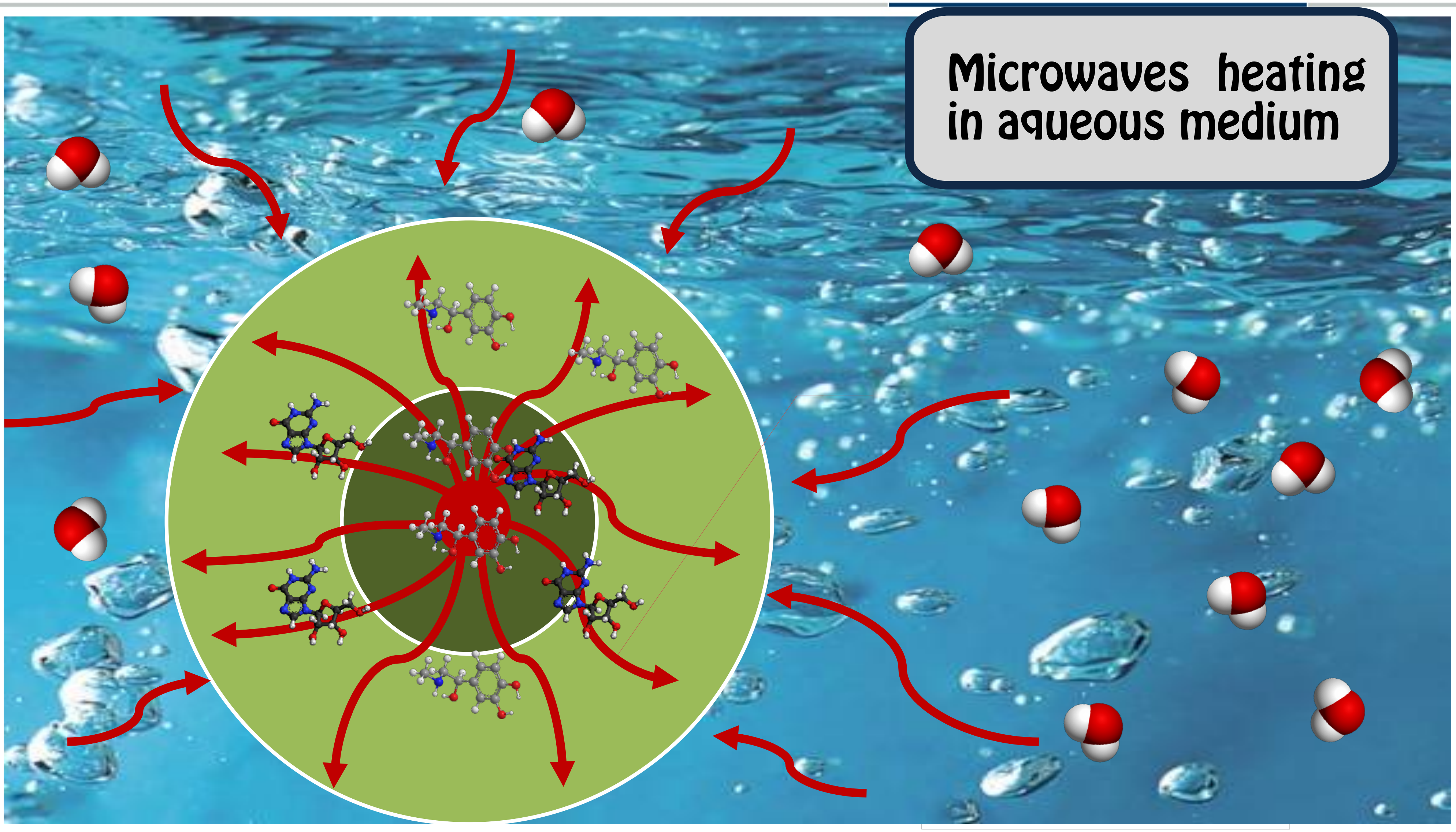


Figure 1: Production methods to obtain carbon materials including top - down and bottom – up approaches.

(Shams, R. Zhang, et al. 2015; Kumar et al. 2016; Niino et al. 2016; Zhang & Yu 2015; Georgakilas et al. 2015; Zhang et al. 2015; Speltini et al. 2013)

Introduction



(Pham et al. 2015; Kruse et al. 2013; Nizamuddin et al. 2017; Asha Jhonsi & Thulasi 2016)

(Shuttleworth et al., 2012; Wu et al., 2014; Li et al., 2017; Zhang et al., 2017)

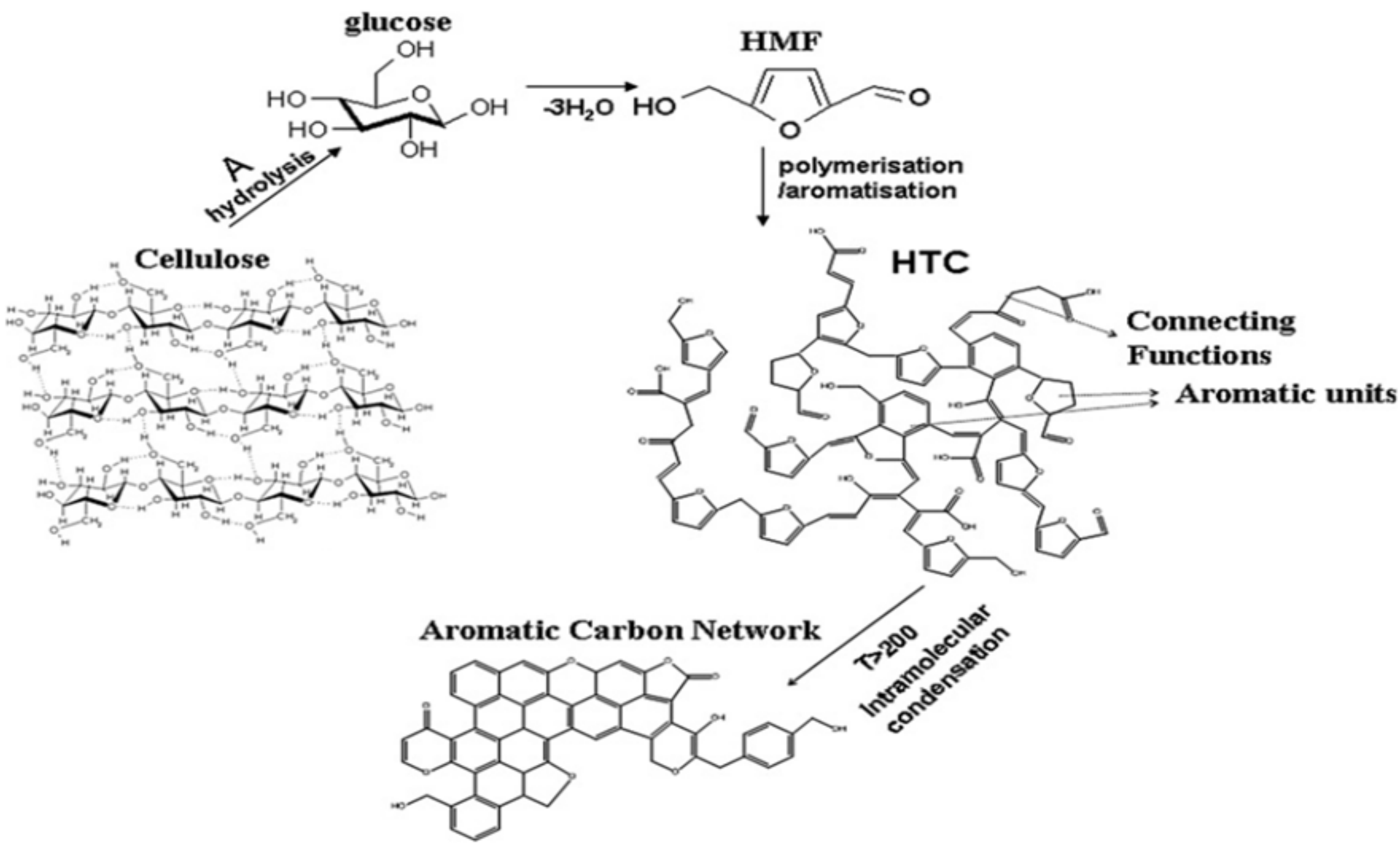
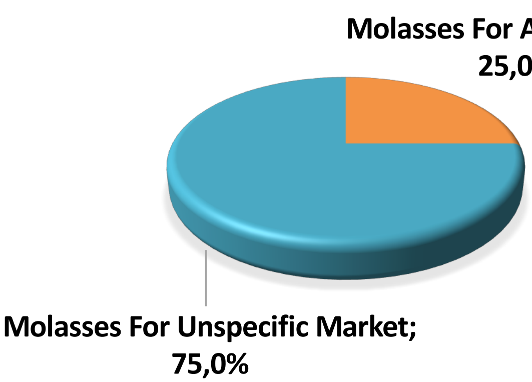


Figure 2: Aromatic carbon network formation mechanism.
Source: Titirici, 2012.

Introduction



beets (*Beta vulgaris*)

Methodology

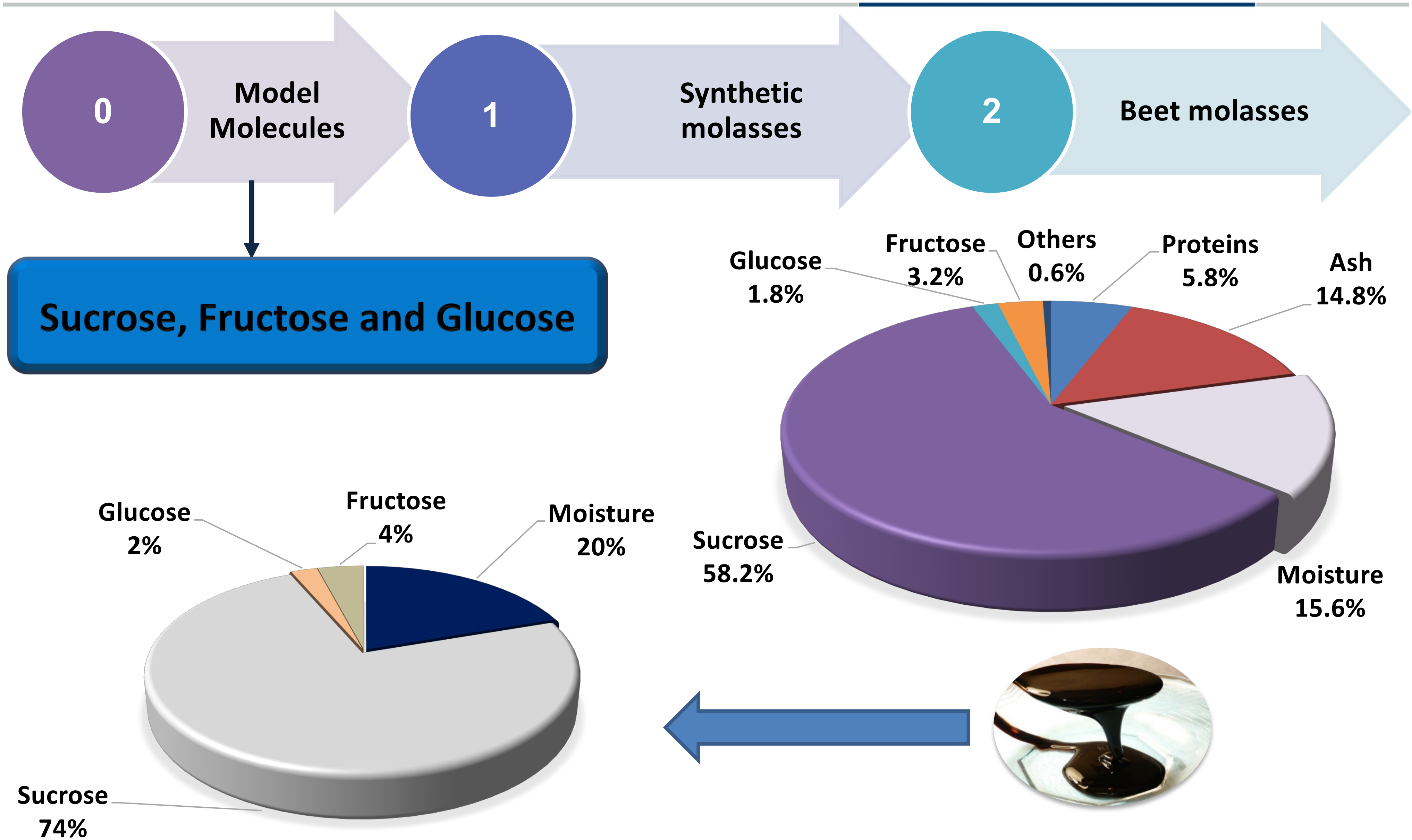


Figure 3: Beet molasses and synthetic molasses composition

Methodology

Carbon spheres Synthesis

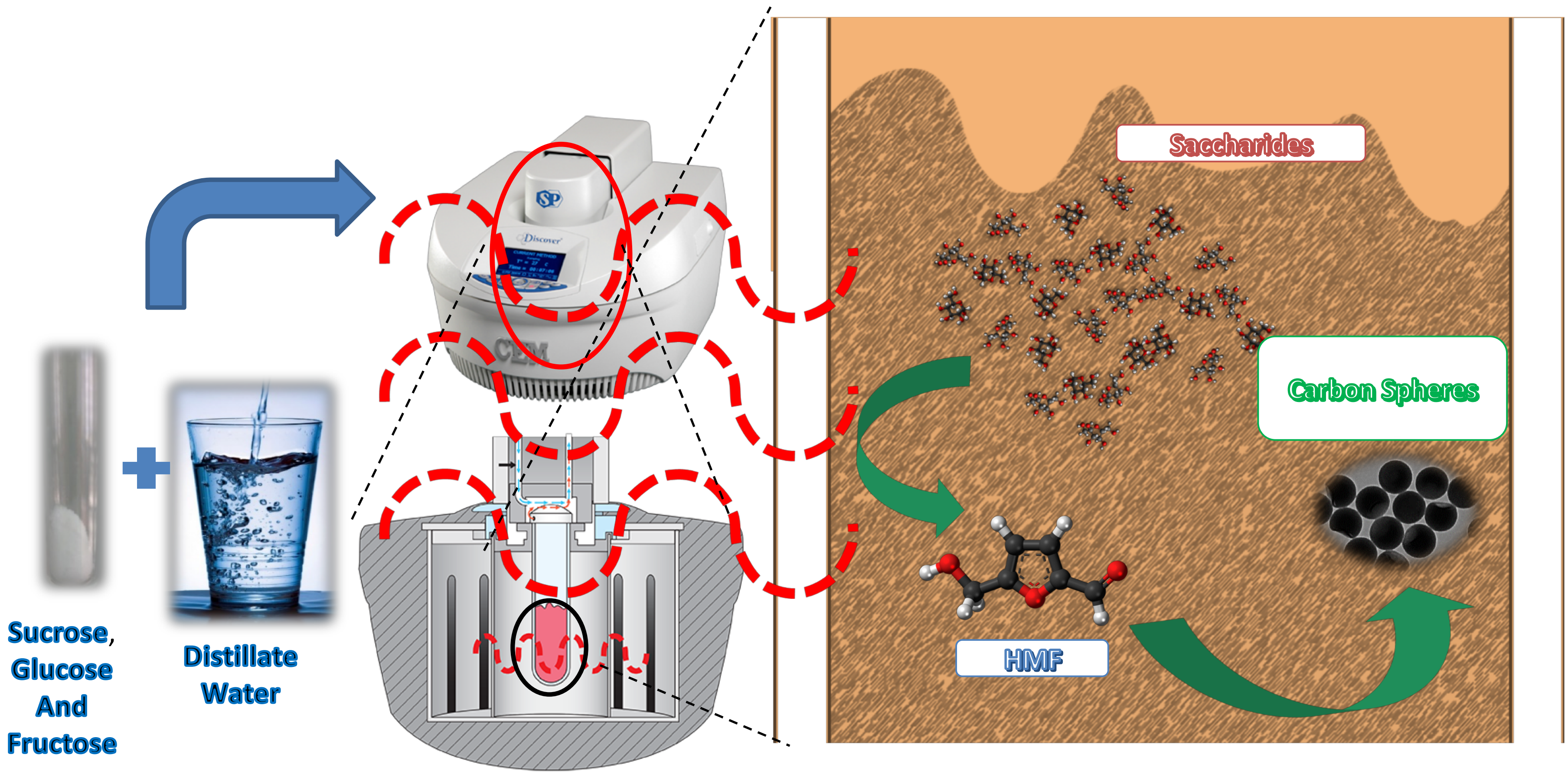


Figure 5: Schematic synthesis of carbon spheres.

Table 1: Factorial design using for evaluate effect of different factors in production of carbon spheres.

Factor	Levels		
	-1	0	+1
Reaction Temperature (°C)	150	165	180
Reaction time (min)	5	22,5	40
Microwave Power irradiation (W)	200	250	300
Water content (%)	60%	75%	90%

For evaluate power irradiation, water content, temperature and time effect was made a factorial design.

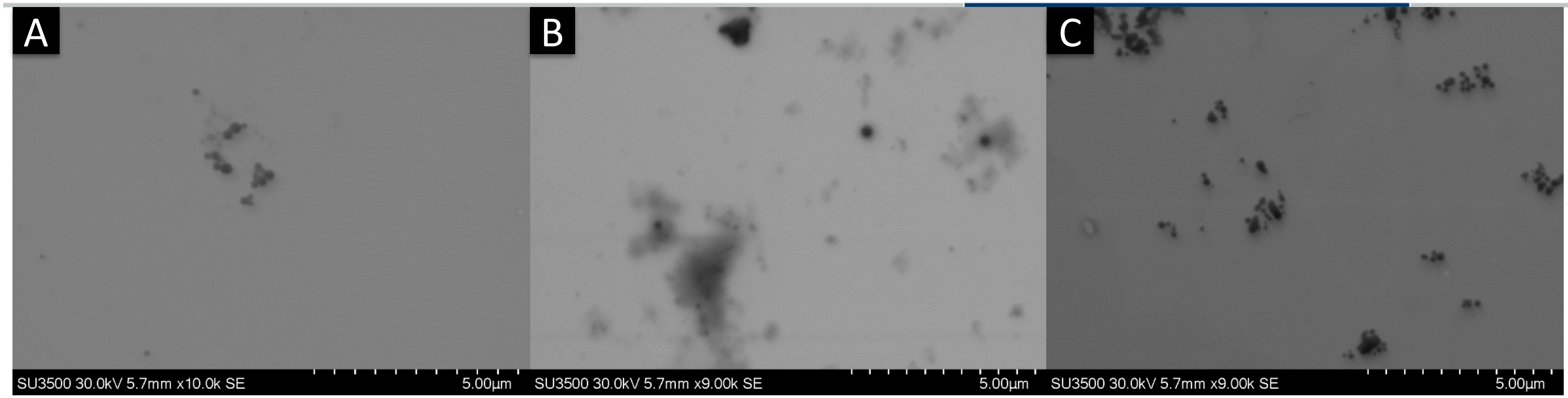


Figure 4: Carbon Spheres obtained by microwave assisted hydrothermal carbonization (MA-HTC) at 5 minutes using 200 W of power with 75% water content from Sucrose (A), Glucose (B) and Fructose (C).

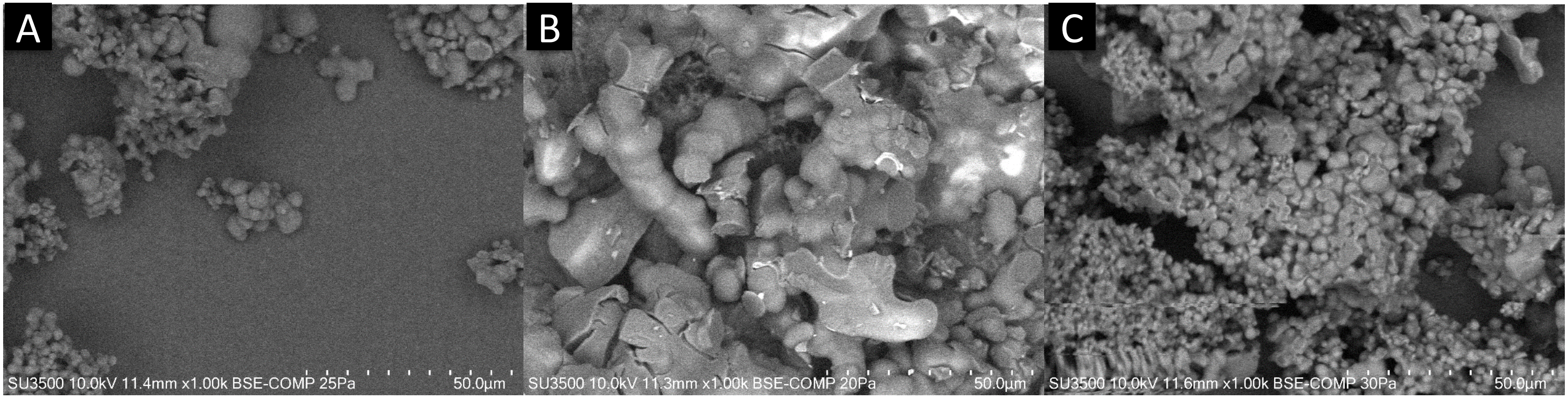
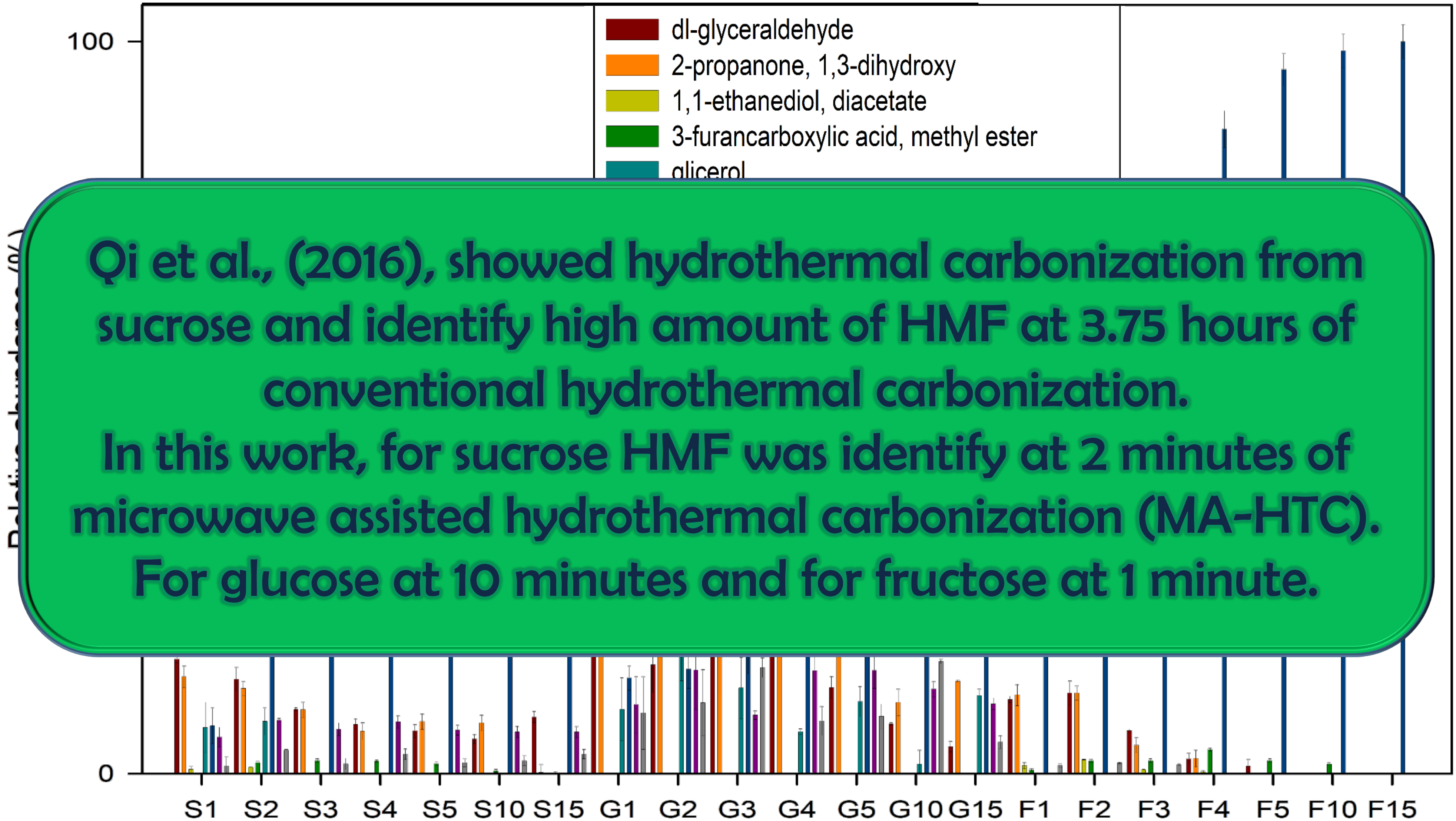


Figure 5: Spherical hydrochar obtained by microwave assisted hydrothermal carbonization (MA-HTC) at 15 minutes using 200 W of power with 75% water content from Sucrose (A), Glucose (B) and Fructose (C).



Qi et al., (2016), showed hydrothermal carbonization from sucrose and identify high amount of HMF at 3.75 hours of conventional hydrothermal carbonization.
In this work, for sucrose HMF was identify at 2 minutes of microwave assisted hydrothermal carbonization (MA-HTC).
For glucose at 10 minutes and for fructose at 1 minute.

Figure 6: MA-HTC for model molecules. Compound indentified.

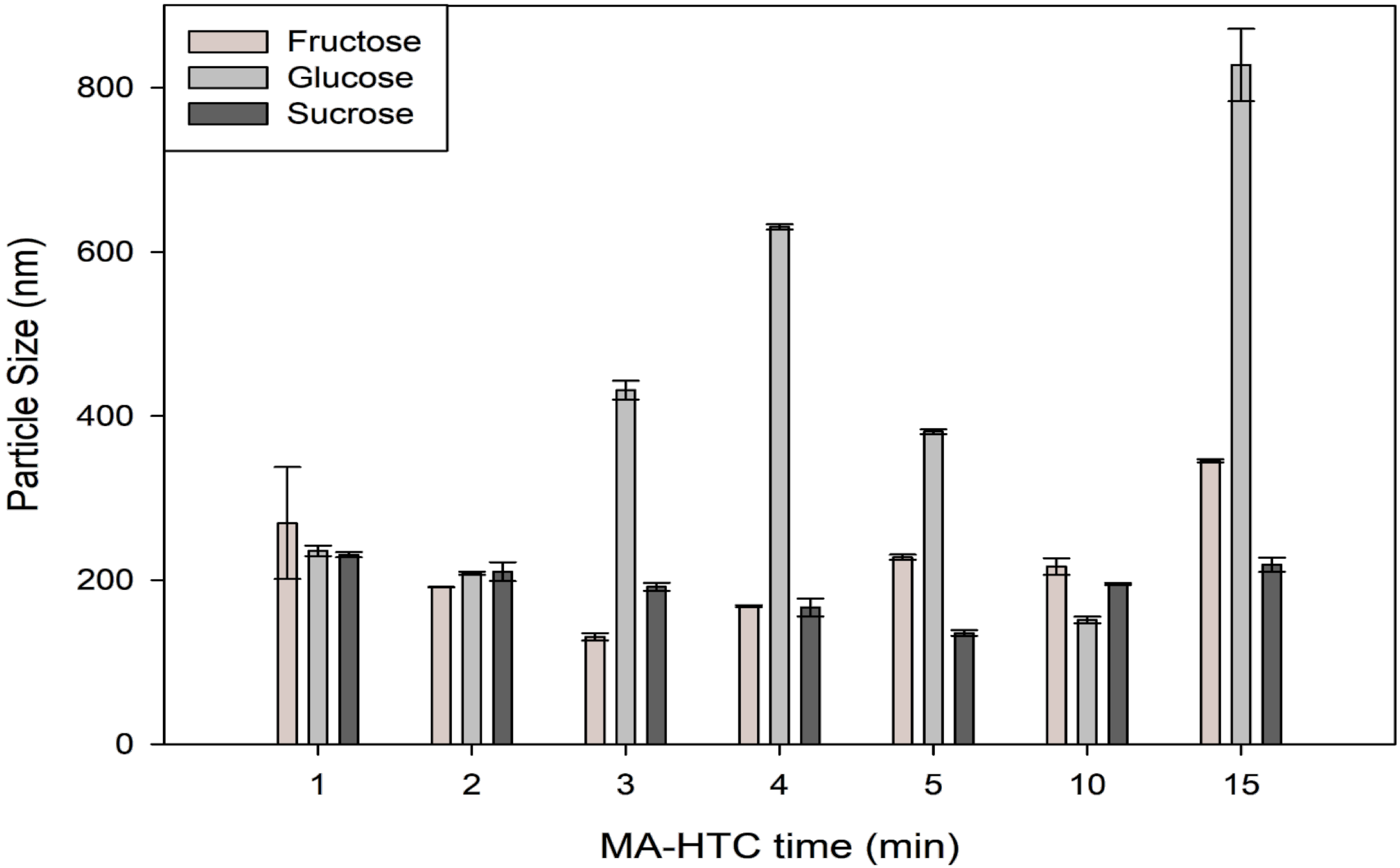


Figure 7: Particle size of carbon spheres produced from sucrose, glucose and fructose at different times process.
Operational conditions: 180°C, 200 W, 300 PSI and 75% of water content.

Synthetic molasses results

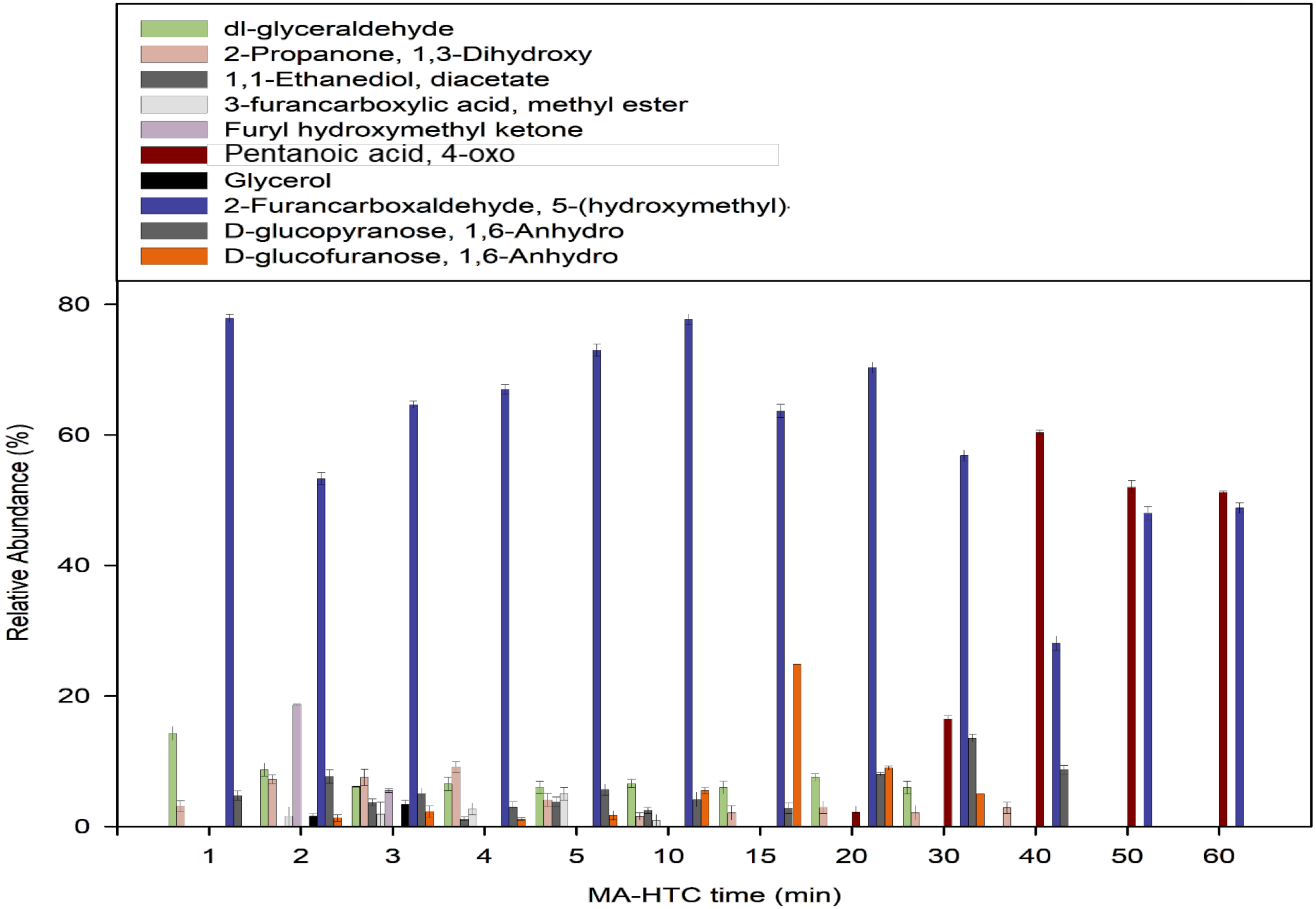


Figure 8: Compounds identified from synthetic molasess treat by MA-HTC.

Synthetic molasses results

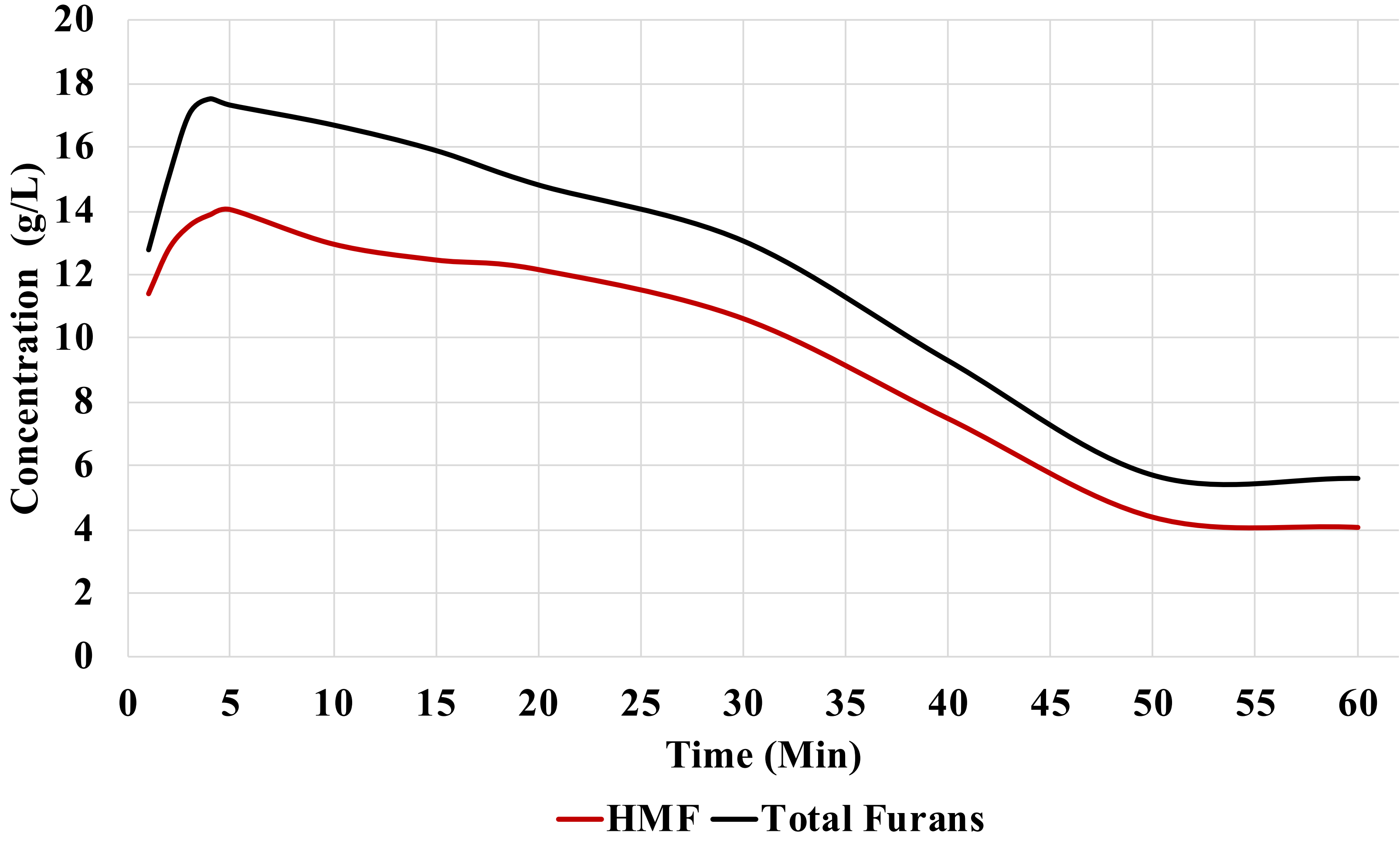


Figure 9: Time study of HMF formation obtained from synthetic molasses.

Synthetic molasses results

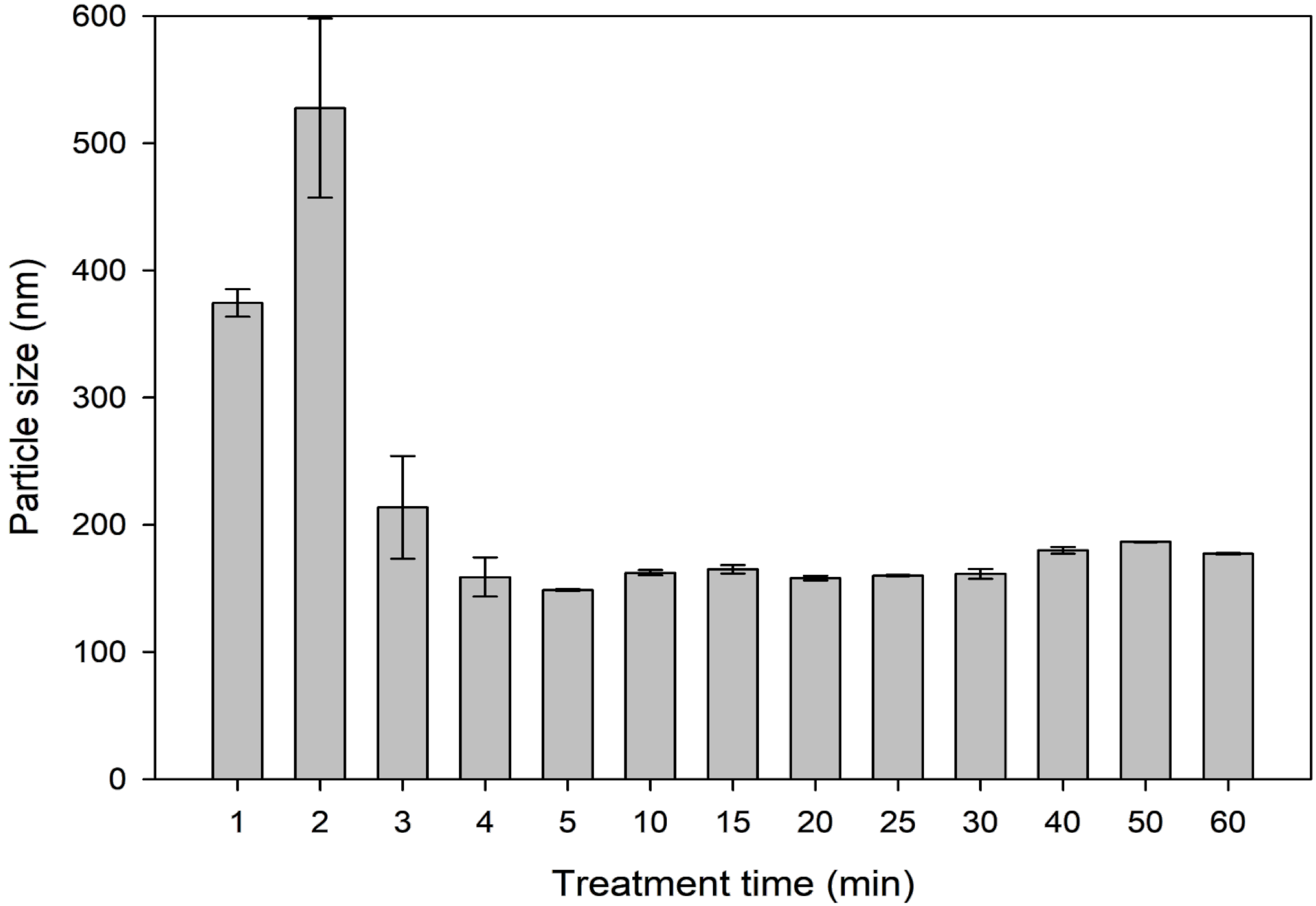


Figure 10: Particle size of carbon spheres produced from synthetic molasses at different times process. Operational conditions: 180°C, 200 W ,300 PSI and 75% water content

Synthetic molasses results

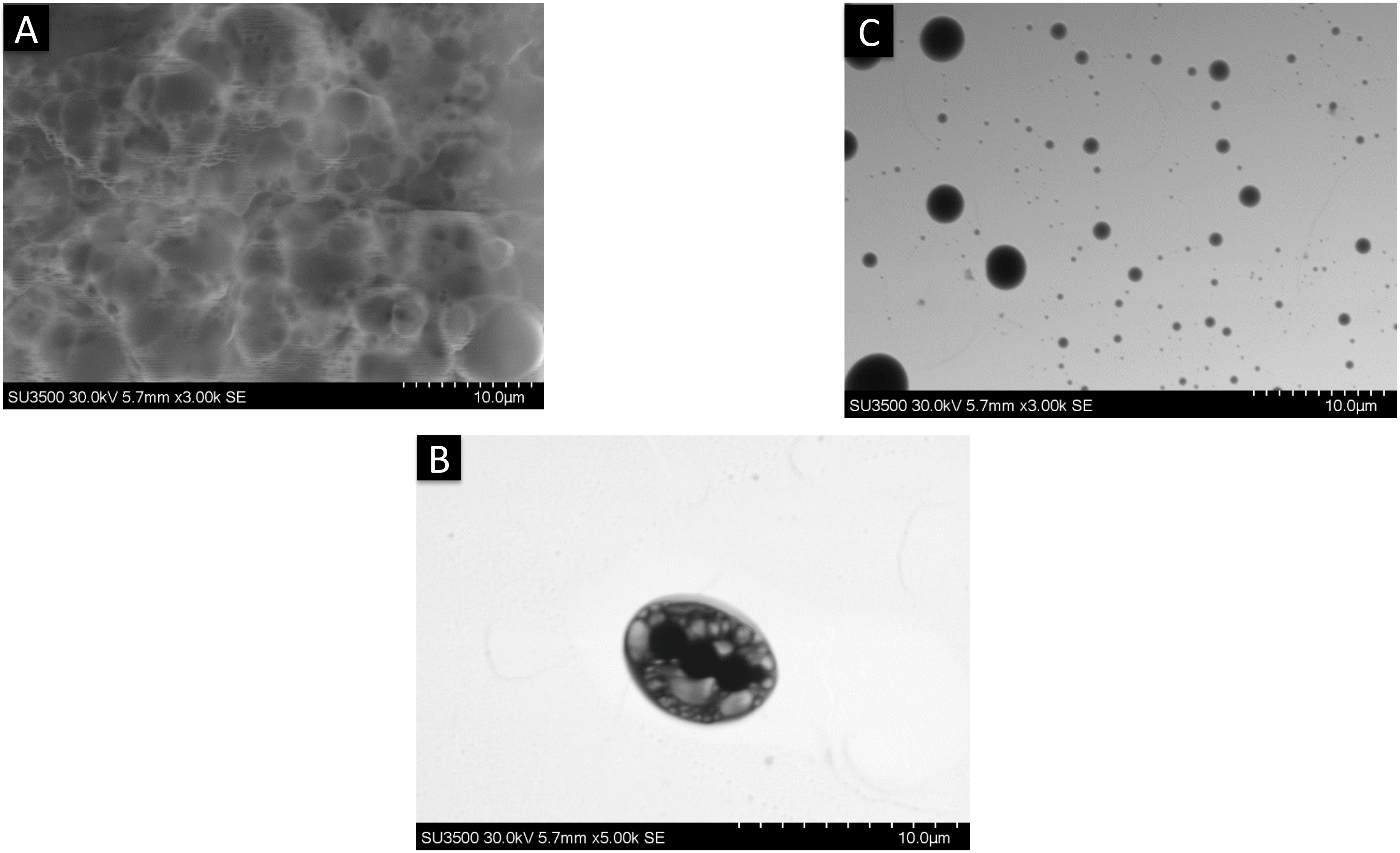


Figure 11: Carbon spheres formation mechanism. A, B and C. Carbon spheres from synthetic molasses using 200 W and 180°C at 1, 3 and 5 minutes.

Synthetic molasses results

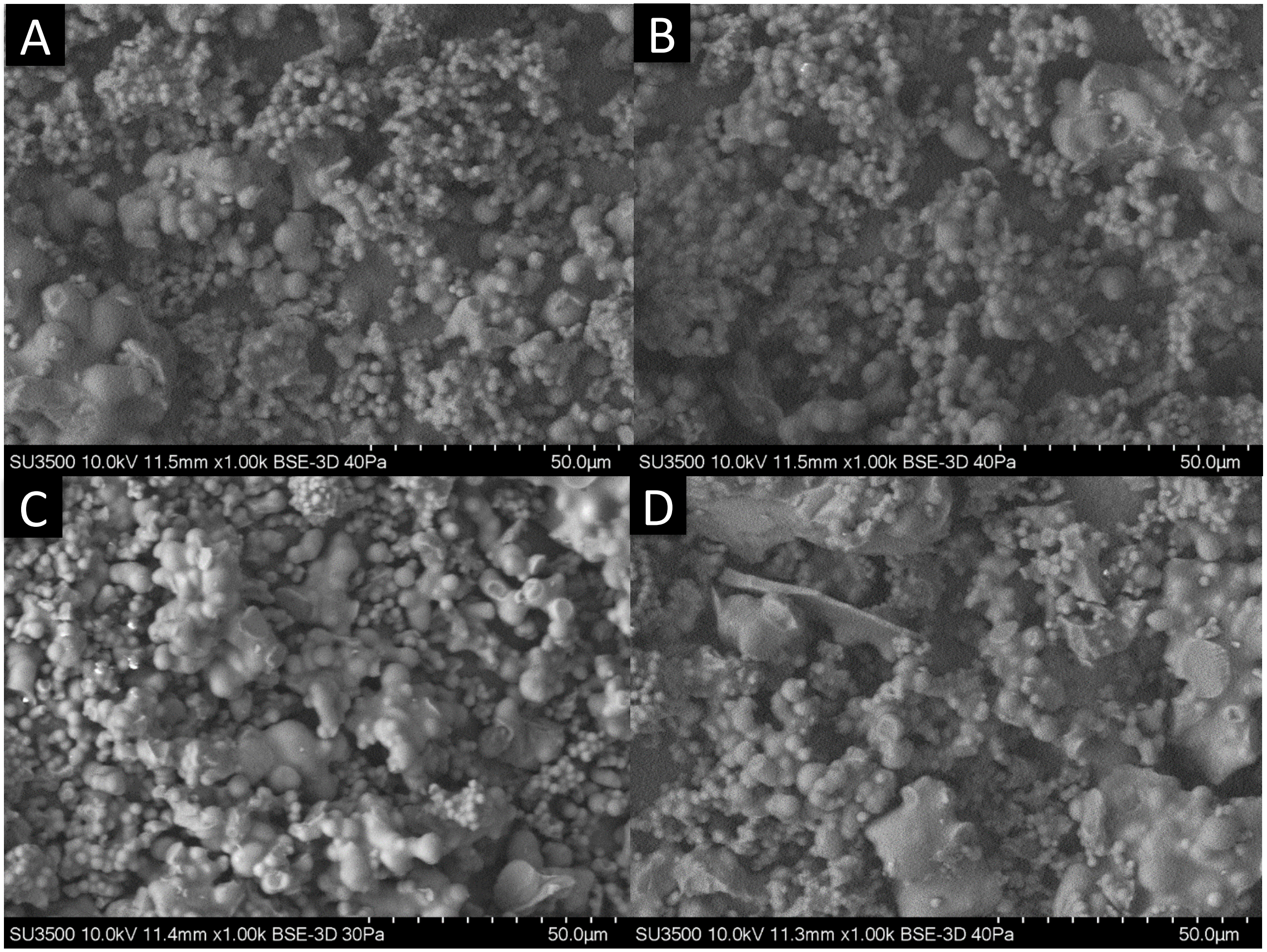


Figure 12: Spherical hydrochar obtain by MA-HTC. Time study using Temperature: 180°C, Power irradiation: 200 W, Water content: 75%. A. 10 minutes. B. 20 minutes. C. 40 minutes. D. 60 minutes.

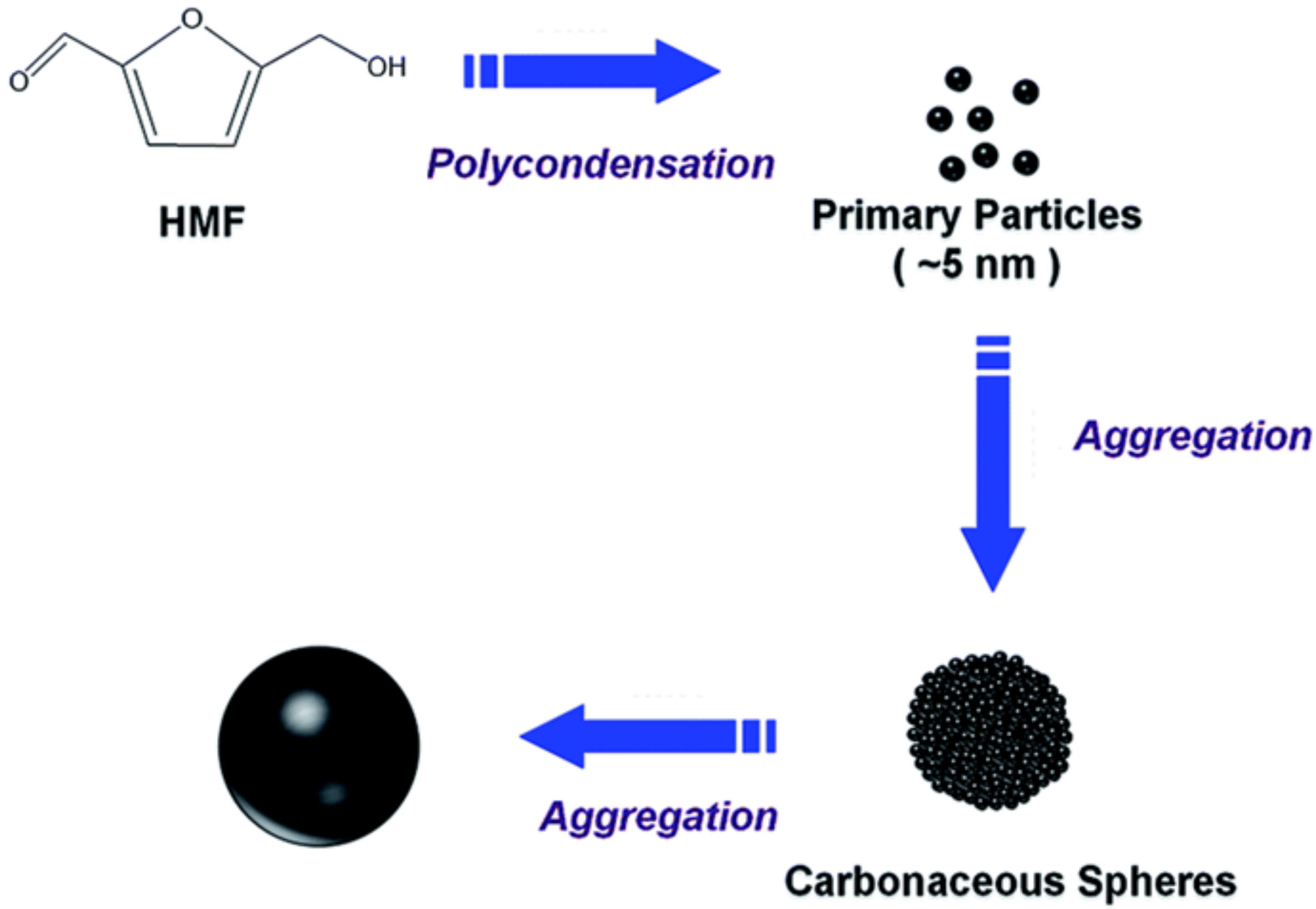


Figure 13: Carbon spheres formation mechanism from carbohydrates
Source: Qi et al., 2016.

Factorial design results

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	2.654E+006	7	3.792E+005	508.66	< 0.0001	significant
A-Temperature	*2.060E+005*	*1*	*2.060E+005*	*276.29*	*< 0.0001*	
B-Power irradi	*6.957E+005*	*1*	*6.957E+005*	*933.25*	*< 0.0001*	
C-moisture	*769.58*	*1*	*769.58*	*1.03*	*0.3231*	
D-Time	*6.612E+005*	*1*	*6.612E+005*	*886.92*	*< 0.0001*	
AB	*1.865E+005*	*1*	*1.865E+005*	*250.22*	*< 0.0001*	
AC	*6.231E+005*	*1*	*6.231E+005*	*835.84*	*< 0.0001*	
AD	*2.811E+005*	*1*	*2.811E+005*	*377.08*	*< 0.0001*	
Curvature	1.781E+005	1	1.781E+005	238.86	< 0.0001	significant
Pure Error	13418.46	18	745.47			
Cor Total	2.846E+006	26				

R^2: 0.9950

Model is AS=17586.436 – 98.548*T – 22.800*PI – 117.783*WC – 77.511*t + 0.118*T*PI + 0.716*T*WC + 0.4122*T*t.
Where AS: Average size; T: Temperature; PI: Power Irradiation; WC: Water Content; t: time.

Factorial design results

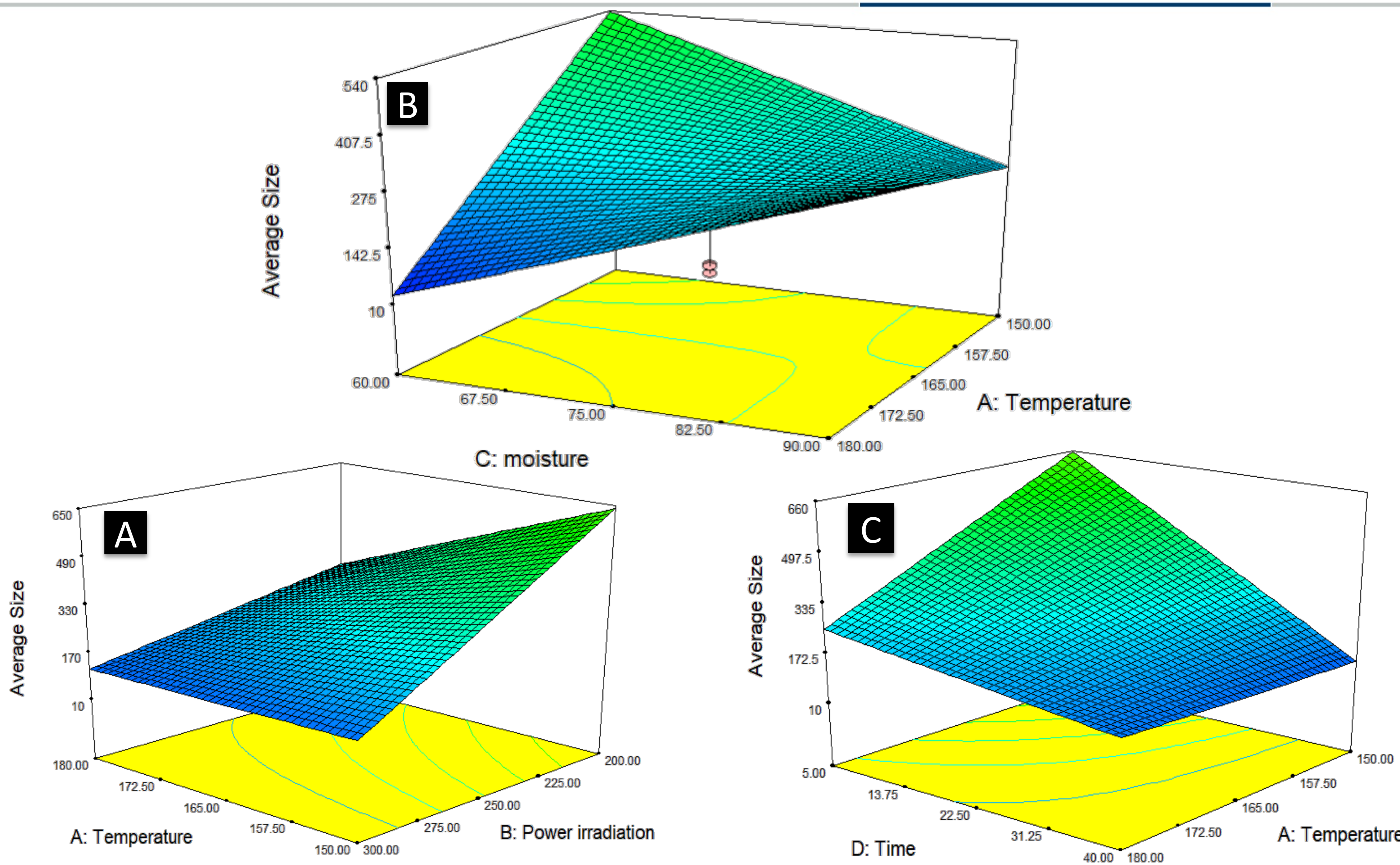


Figure 14: 3D - Graphical effect in production of carbon spheres from synthetic molasses.

Average particle size: 5.9 nm.

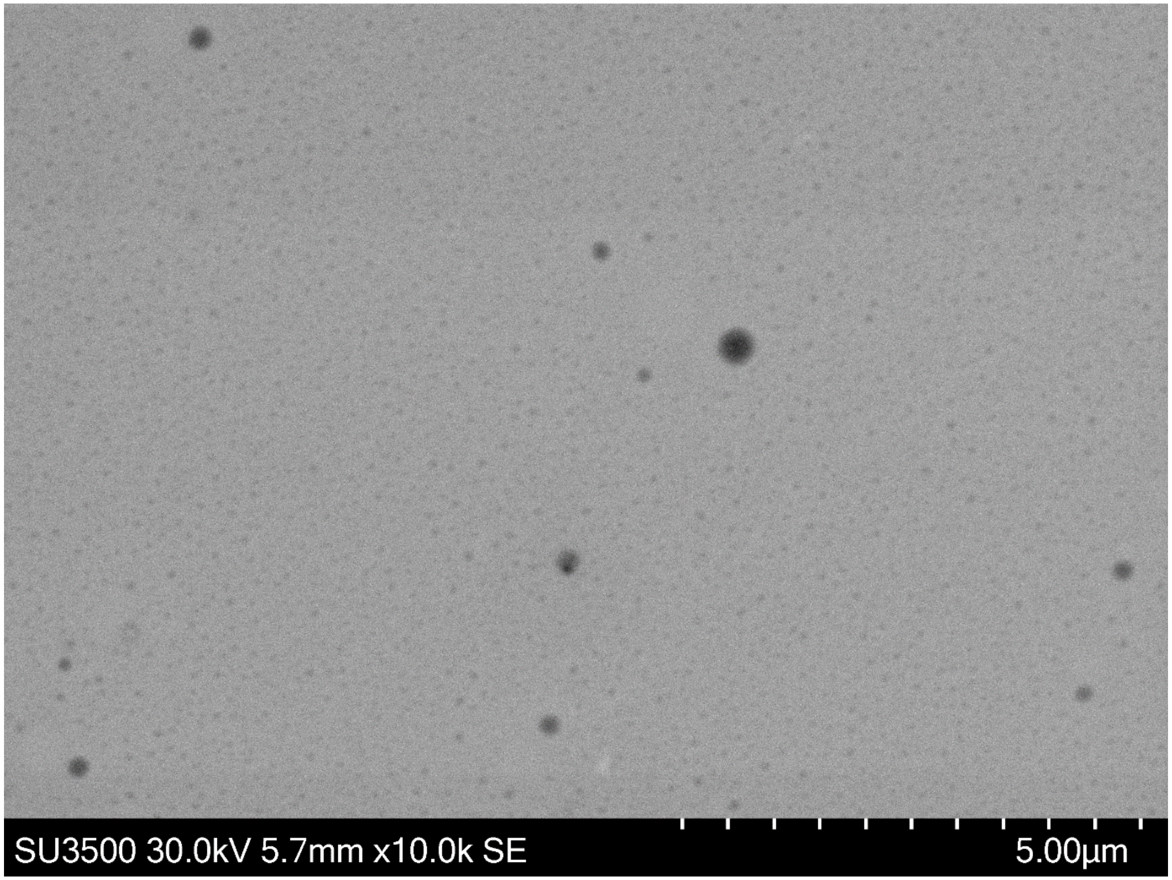


Figure 15: RUN 23. Carbon spheres from synthetic molasses at 5 minutes, 300 W, 60% water content and 180°C.

Conclusions

- **Microwave-assisted hydrothermal carbonization proves to be a fast and efficient strategy for generating carbon materials from carbohydrates.**

- **The study of the formation time of carbon spheres from the model molecules showed serious differences in formation time and intermediary compounds. Fructose turns out to be the model molecule that transforms fastest into HMF and thus into suspended carbon spheres. Additionally, the particles generated by fructose generate spherical hydrochar less agglomerated than glucose and sucrose.**

Conclusions

- Regarding the time study of synthetic molasses, this showed that HMF is produced in short periods of time without the addition of a catalyst, this may be due to the synergy effect generated by using water as a reaction medium and the effect of microwave energy. The microwave energy generates a constant change of the dipoles together with the migration of ions create friction within the material and this internal energy, which is dispersed in the form of heat, causes most of the material to heat up. Additionally, working in subcritical conditions generates a protonation in the medium, generating acidification, which favors the formation of HMF. On the other hand, very long times (20 minutes) favor the decomposition of HMF in levulinic acid.

- On the other hand, the experimental design showed that power, water content and the combined effect between temperature and time are fundamental to obtain carbon nanoparticles, including carbon dots.

Future Work

- According to the above, future work should focus on the stabilization of particles in the medium, slowing down the mechanism of aggregation of carbon spheres. Additives, such as nitrogen compounds can be used for this and it is for this reason that the next step is to add to the synthetic molasses, the nitrogenous components of sugar beet molasses.

- Finally, this study shows that microwave technology not only allows the synthesis of carbon nanoparticles, but could also be oriented to obtain other value-added products such as HMF or levulinic acid, among others.

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