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Microwave-assisted furfural synthesis from D-xylose in the presence of NaCl: Comparison of microwave heating with conventional heating

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SUPPORTING INFORMATION

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1. Materials

D-(+)-xylose (≥99%) and Sodium chloride (≥99.5%) were purchased from Sigma-Aldrich. Hydrochloric acid (37.5%) was purchased from J.T. Baker. The solutions were prepared with ultrapure (MilliQ) water.

2. Methods

2.1 Solution preparation

The required amount of xylose and sodium chloride were weighted into a 50 mL beaker and dissolved in ultrapure water. After rigorous stirring for 10 minutes to ensure homogeneous concentration, the solution was transferred to a 100 mL volumetric flask. Then, the required amount of hydrochloric acid was measured into the flask by a glass pipette. The volumetric flask was filled up to 100 mL with ultrapure water, shaken for 10 minutes and stored in the fridge overnight. Shortly prior to the experiments, the solution was brought at room temperature while stirred.

2.2 Microwave reactors

Two microwave platforms were used to perform the experiments. The CEM Discover was used for the NaCl concentration experiments and the Anton Paar Monowave 300 was used for the rest

of the experiments. Both are single-mode microwave reactors and operate at 2.45 GHz. However, significant differences with regard to automation, vessel design, safety features, temperature and pressure monitoring and power output are present. While the maximum output power or the CEM Discover is rated at 300 W, the Anton Paar Monowave 300 can provide 850 W of continuous microwave power. The maximum pressure of the CEM Discover is 20 bar, while the Anton Paar system can operate at 30 bar pressure. Furthermore, both systems are equipped with IR sensors for real-time temperature measurements, but the Anton Paar Monowave 300 instrument has an extra, ruby-based optical fiber thermometer as well, which is immersed in the reactor vessel. Important for this study is that apart from the three borosilicate (glass) vessel types (4, 10 and 30 mL), a special 10 mL silicon carbide (SiC) vessel is available for the Anton Paar system (Figure S1). By using this strongly microwave absorbing material, specific/non-thermal microwave effects can be studied. Prior to the experiments, the built-in infrared sensor of the CEM Discover system was calibrated to the required reaction temperature and vessel by means of a FISO fiber optic sensor using ethylene glycol anhydrous (99.8%) and glycerol (≥99.5%) in an open reactor. In all other cases, the sample vials were capped.

Figure S1. Glass and SiC vials available for the Anton Paar Monowave 300 microwave reactor. Both vials have the same geometry.

The thermophysical properties of the two vials are presented in Table S1.

Table S1. Comparison of the thermophysical properties of borosilicate (glass) and SiC vials [1].

Property	Unit	SiC (EKasicF)	Borosilicate
Thermal Conductivity	λ [W $m^{-1}K^{-1}$]	125	1.2
Thermal Expansion Coeff.	α [K^{-1}]	$4.1*10^{-5}$	$3.3*10^{-6}$
Specific Heat Capacity	C_p [J $g^{-1}K^{-1}$]	0.6	0.7
Density	ρ [g mL^{-1}]	3.10	2.23
Thermal Effusivity	E [J $s^{-1/2}m^{-2}K^{-1}$]	15000	1400

3. Results

3.1 Xylose conversion and furfural yield in the glass and SiC vials

Kinetic modelling

The measured experimental results in terms of xylose and furfural concentration were fitted, using least square regression, to the kinetic model equations, described in the main paper, in order to derive the first order kinetic parameters k_1, k_2 and k_3. The model is in a very good agreement with the experimental data and the results are presented in Figure S1.

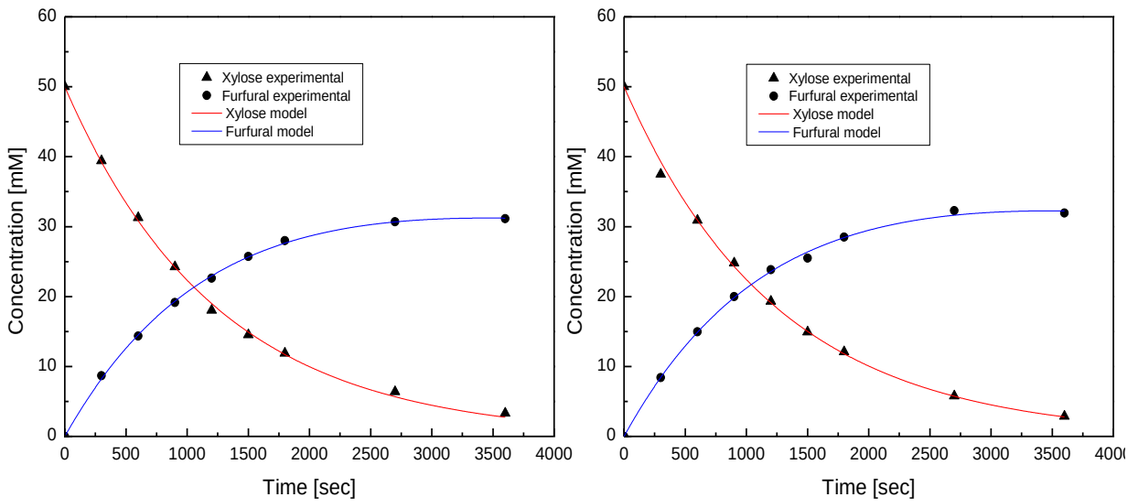

Figure S1: Analytical results of the microwave (glass vial) and conventional (SiC vial) heating experiments at 170 °C (xylose: 50mM, HCl: 50mM, NaCl: 500mM, stirring at 600rpm) at different residence times, fitted in first order kinetic model equations to derive the kinetic parameters. Red and blue lines are the kinetic model estimations. Right: SiC vial. Left: Glass vial.

3.2 Heating experiments in the SiC vial

In this report it has been speculated that the strongly absorbing SiC vials, will effectively shield the reaction mixture from interacting with the applied microwave field. To confirm this hypothesis, heating experiments of two solvents with vastly different dielectric properties (tanδ) were performed. The experiments were performed under constant microwave power and the heating profiles obtained in the standard Pyrex vial were compared with the profiles obtained in the SiC vessel. Some properties of the two solvents chosen, namely ethanol and toluene, are presented in Table S2. Ethanol with a loss tangent of 0.941 couples very well with the microwaves, while toluene with a loss tangent of only 0.040 is a very poor microwave absorber. In these heating experiments, 4 mL of each solvent were heated using the Anton Paar Monowave 300 first in the Pyrex vial and then in SiC vial. The microwave power was constant at 100 W for all experiments and was applied for 30 seconds. Stirring was employed at a stirring speed of 600 rpm and temperature was measured by the internal fiber optic sensor of the device.

Table S2. Properties of toluene and ethanol

Property	Toluene	Ethanol
Boiling point at 1 bar [°C]	110.6	78.4
Density at 1 bar and 25 °C [g/mL]	0.863	0.789
Specific heat capacity at 25 °C [J/mol K]	157.1	112.4
Loss tangent	0.040	0.941

By examining the results in Figure S2, it appears that when the microwave transparent Pyrex vial is employed, the heating profiles of the two solvents follow the expected trend, in relation with their tanδ values, with ethanol heating at a much faster rate than toluene. However, when the SiC vials are employed the two solvents heat at a very comparable rate, regardless to their tanδ values. The fact that the very strong absorbing ethanol heats at a very comparable rate with the poor microwave absorbing toluene, when placed inside the SiC vial, indicates that the field intensity inside the SiC vial must be very low. Hence, it can be safely assumed that heating occurs mostly by means of conventional heat transfer mechanisms and not by dielectric heating effects.

Based on this evidence, the SiC vessels are considered to effectively shield their contents (reaction mixture) from the microwave field, enabling the reaction to be conducted under conventional heating, but inside the microwave reactor. This allows for excellent heating rates and process control features inherit to microwave reactors [1].

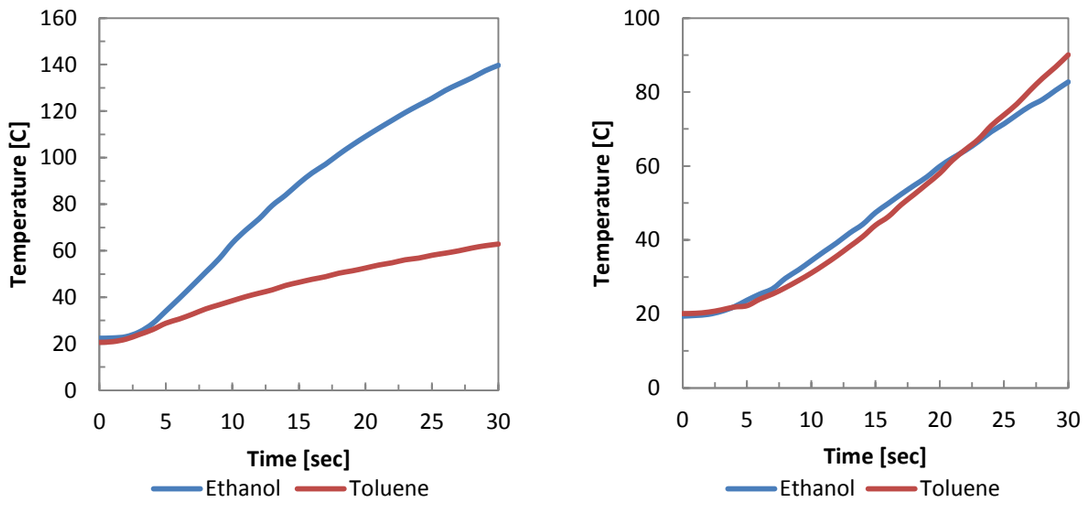

Figure S2. Heating rates for ethanol and toluene in the standard Pyrex vial (left) and in the SiC vial (right) at 100 W microwave power for 30 seconds (Single mode microwave irradiation, stirring at 600 rpm, internal fiber optic temperature measurement). Comparable heating rates for toluene (tanδ = 0.040) and ethanol (tanδ = 0.941) in the SiC, indicates that field intensity inside the SiC is very low.

REFERENCES

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