**Microfluidic reactor development for isothermal kinetic measurements of sugars hydrolysis and global kinetics determination by model-fitting approach**

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**Supplementary Data**

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# S1. Thermophysical properties of the diphasic system

Precise thermophysical properties such as viscosity, density, thermal conductivity, and heat capacity of the two fluids, water and PDMS, were obtained from the National Institute of Standards and Technology. Although, glucose or cellobiose was dissolved into the water, their presence, and their influence on thermophysical properties were neglected.

For the water, the lowest and highest values of thermophysical properties were selected to clearly define what the variation entails in the operating data range.

At 12 bar and 23°C, = 998.04 kg/m3 and μ = 932 µPa.s

At 70 bar and 23°C, = 1000.6 kg/m3 and µ = 931 µPa.s

At 12 bar and 180°C, = 879.6 kg/m3 and μ = 144.6 µPa.s

At 70 bar and 180°C, = 883.6 kg/m3 and µ = 146.0 µPa.s

At 54 bar and 260°C, = 772.9 kg/m3 and μ = 98.9 µPa.s

At 70 bar and 260°C, = 775.1 kg/m3 and µ = 99.5 µPa.s

We considered an average reaction pressure of 40 bars

At 40 bar and 180°C, = 889 kg/m3

At 40 bar and 260°C, = 787 kg/m3

The heat capacity in J/mol.K of the water at T (in K/1000) was deduced from the following equation[1]:

where A = -203.6060, B = 1523.290, C = -3196.413, D = 2474.455 and E = 3.855326

And the thermal conductivity in W/(m.K) from the equation[2]:

λ =

For the PDMS, the density in kg/m3 was determined from density measurements of Clearco 20 cSt PDMS[3]

where T, the temperature is in degree Celsius.

# S2. 3D sectional view of the microfluidic reactor

Une image contenant capture d’écran, Rectangle, conception

Description générée automatiquement

Figure S1. 3D sectional view of the reactor

# S3. Pre-experimental study on phase changes in microfluidic reactor

The original idea of the experimental work on the microfluidic reactor was to measure both the kinetics and evaporation rate of a solution of glucose during fast heating under near isothermal conditions. We started off by using a two-phase flow of nitrogen (gas) and glucose solution (liquid). The concentration of glucose in the product stream as well as the deviation percentage between repeat runs at 300°C are shown in Table S2 for different gas and liquid flow rates. It was clear that the repeatability of these experiments was not good and some of the deviation percentages were as high as 63%. Originally, we suspected that the bad repeatability was due to upsets in the system’s steady state during the experiments, however by installing a logger on the back pressure pump we were able to monitor the pressure and observed no deviation in pressure. By taking some films during the experiments we finally realized that there was a change in velocity of the slugs in the heated section, and this change was not regular. This explained why our kinetic measurements were not repeatable.

To solve this issue, the next idea was to replace the nitrogen gas by a liquid with a high boiling point in order to make the slugs (of the glucose solution) move through the heated section at a constant velocity. We selected PDMS (polydimethylsiloxane) for this purpose due to its high boiling point (220°C) and immiscibility with the aqueous glucose solution.

Some runs were then carried out at 200°C and a film was taken to monitor the velocity of the glucose solution slugs. The film demonstrated that during evaporation, the large volume expansion of the glucose slug (1600 times) is so large that the evaporated vapour shoots into the PDMS liquid slugs and causes a mixture of PDMS and gas (Figure S1b), the velocity of which is not possible to control. Figure S1 shows the slug flow in the cold- (Figure S1a) and heated sections (Figure 1b) of the reactor.

After these tests, we also calculated that when a liquid slug with a diameter of 150 µm and length of 99 µm (measured using the high-speed camera) evaporates, it requires 16 cm of length in the capillary to account for its volume expansion. This further proved to us that we could not avoid mixing with the oil, neither could we achieve robust control of the slug velocity.

We therefore concluded that the kinetic measurements needed to be performed under conditions were there is no phase change, and it is possible to control the slug velocity.



a

b

Figure S2. Slug flow of PDMS and glucose solution in the cold (a) and heated (b) sections of the microfluidic reactor

# S4. HPLC calibration curves

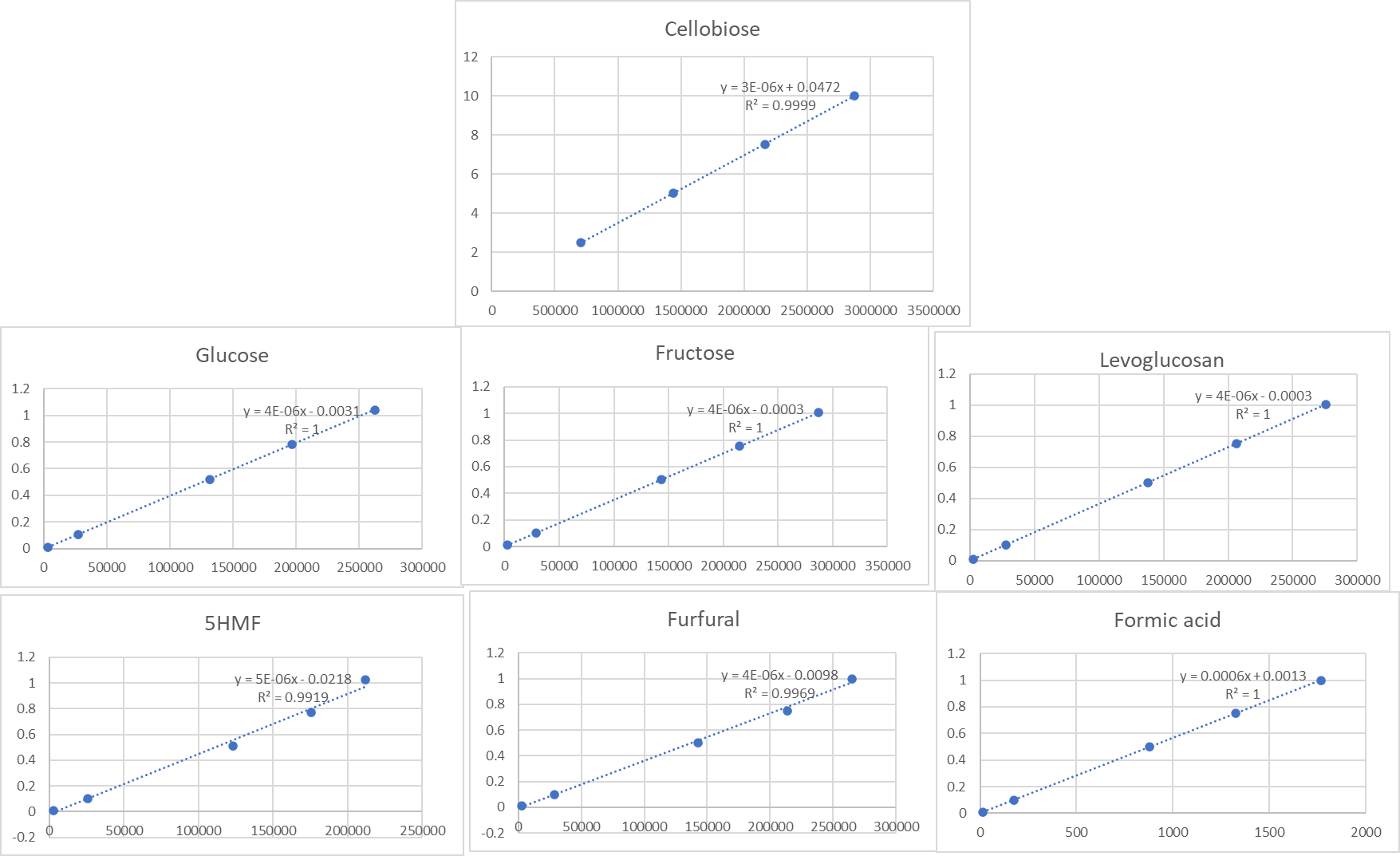


Figure S3. HPLC calibration curves

# S5. Repeatability of experimental runs

Each experimental run was repeated 3 times, and the average, standard deviation and percentage deviation are shown in Table S1 for glucose and Table S2 for cellobiose. The maximum deviation was determined to be 3.3% for glucose and 5.4% for cellobiose.

Table S1: Repeats of glucose runs

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | | Glucose concentration (g/L) | | |  | | |
| Temperature (°C) | Reaction time (s) | Run 1 | Run 2 | Run 3 | Average | Standard deviation | % deviation |
| 180 | 5 | 11.3 | 11.3 | 11.3 | 11.3 | 0.0 | 0.0 |
| 180 | 10 | 11.2 | 11.2 | 11.2 | 11.2 | 0.0 | 0.1 |
| 180 | 20 | 11.1 | 11.1 | 11.1 | 11.1 | 0.0 | 0.2 |
| 180 | 50 | 9.4 | 9.5 | 9.4 | 9.4 | 0.1 | 0.6 |
| 180 | 80 | 9.3 | 9.4 | 9.5 | 9.4 | 0.1 | 1.2 |
| 210 | 5 | 11.2 | 11.2 | 11.2 | 11.2 | 0.0 | 0.0 |
| 210 | 10 | 11.0 | 11.1 | 11.0 | 11.0 | 0.0 | 0.1 |
| 210 | 20 | 10.7 | 10.7 | 10.7 | 10.7 | 0.0 | 0.1 |
| 210 | 50 | 8.3 | 8.4 | 8.4 | 8.3 | 0.1 | 0.8 |
| 210 | 80 | 7.3 | 6.9 | 7.4 | 7.2 | 0.2 | 3.3 |
| 240 | 5 | 10.6 | 10.6 | 10.6 | 10.6 | 0.0 | 0.1 |
| 240 | 10 | 10.0 | 10.0 | 9.9 | 10.0 | 0.0 | 0.3 |
| 240 | 20 | 7.6 | 7.6 | 7.6 | 7.6 | 0.0 | 0.1 |
| 240 | 50 | 6.1 | 6.2 | 6.2 | 6.1 | 0.1 | 1.1 |
| 240 | 80 | 4.9 | 5.2 | 5.1 | 5.0 | 0.1 | 2.7 |
| 260 | 5 | 10.2 | 10.3 | 10.2 | 10.2 | 0.0 | 0.1 |
| 260 | 10 | 8.7 | 8.7 | 8.7 | 8.7 | 0.0 | 0.1 |
| 260 | 20 | 6.8 | 7.0 | 6.8 | 6.9 | 0.1 | 1.7 |
| 260 | 50 | 4.9 | 4.9 | 4.9 | 4.9 | 0.0 | 0.2 |
| 260 | 80 | 4.2 | 4.3 | 4.3 | 4.2 | 0.1 | 1.4 |

Figure S4: Concentration versus residence time for glucose hydrolysis.

Table S2: Repeats of cellobiose runs

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | Cellobiose concentration (g/L) | | |  |  |  |
| Temperature (°C) | Reaction time (s) | Run 1 | Run 2 | Run 3 | Average | Standard deviation | % deviation |
| 180 | 10 | 7.8 | 7.9 | 7.9 | 7.9 | 0.0 | 0.6 |
| 180 | 20 | 7.8 | 7.9 | 7.9 | 7.8 | 0.1 | 0.8 |
| 180 | 50 | 7.8 | 7.8 | 7.9 | 7.8 | 0.0 | 0.2 |
| 180 | 80 | 7.8 | 7.9 | 7.8 | 7.8 | 0.0 | 0.2 |
| 210 | 10 | 8.4 | 8.4 | 8.4 | 8.4 | 0.0 | 0.2 |
| 210 | 20 | 7.9 | 8.0 | 8.0 | 8.0 | 0.1 | 0.9 |
| 210 | 50 | 7.8 | 7.8 | 7.9 | 7.8 | 0.0 | 0.3 |
| 210 | 80 | 7.6 | 7.6 | 7.6 | 7.6 | 0.0 | 0.2 |
| 240 | 10 | 7.4 | 7.4 | 7.4 | 7.4 | 0.0 | 0.0 |
| 240 | 20 | 6.8 | 6.8 | 6.8 | 6.8 | 0.0 | 0.0 |
| 240 | 50 | 5.1 | 5.1 | 5.2 | 5.1 | 0.0 | 0.0 |
| 240 | 80 | 4.5 | 4.5 | 4.5 | 4.5 | 0.0 | 0.0 |
| 260 | 10 | 7.2 | 7.2 | 7.2 | 7.2 | 0.0 | 0.1 |
| 260 | 20 | 6.2 | 6.2 | 6.2 | 6.2 | 0.0 | 0.2 |
| 260 | 50 | 4.6 | 5.0 | 4.5 | 4.7 | 0.3 | 5.4 |
| 260 | 80 | 3.3 | 3.1 | 3.2 | 3.2 | 0.1 | 3.4 |

Figure S5: Concentration versus residence time for cellobiose hydrolysis.

# S6. Mass balance and residence time

Une image contenant texte, diagramme, capture d’écran, ligne

Description générée automatiquement

**Figure S6. Inside the heating device the dilatation of both phase (PDMS and aqueous) leads to an increase of slug’s length (LPDMS and LW) and consequently leads also to increase velocities and decreases the residence time**

Conservation of mass in heated section:

The mass flow rate into the capillary can be expressed according to Eq.:

Equation 1

Equation 2

Equation 3

Equation 4

where is the total mass flow rate and and respectively for water and PDMS, stands for the density at ambient temperature, ν for the speed and S for the capillary section. And the total volume of the diphasic system at , can be expressed in terms of residence time, **,** velocity, v, and section, S; but also, in terms of mass and density at , .

As a result, the residence time can be expressed according to the Equation 5:

**Table S3. Theoretical calculations of residence time and corresponding plug velocity**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Radius of capillary | 1.50×10-4 | m | 1.50×10-4 | m |
| Section | 7.07×10-8 | m2 | 7.07×10-8 | m2 |
| Lenght | 0.22 | m | 0.22 | m |
| Tambiant | 23 | °C | 23 | °C |
| ρH2O (Tamb,12bar) | 998.04 | kg/m3 | 998.04 | kg/m3 |
| ρH2O (Tamb,70bar) | 1000.06 | kg/m3 | 1000.06 | kg/m3 |
| µH2O(Tamb) | 931.5 | µPa.s | 931.5 | µPa.s |
| PH2O | 45.5 | bar | 45.5 | bar |
| Length of pipe between the pump for H2O and reactor | 2 | m | 2 | m |
| Pipe diameter | 8.00×10-4 | m | 8.00×10-4 | m |
| H2O | 1 | mL/min | 1 | mL/min |
| Pressure drop, ΔPH2O pump to reactor | 30.9 | bar | 30.9 | bar |
| ρH2O (Tamb, PH2O) | 999.206724 | kg/m3 | 999.206724 | kg/m3 |
| Treac | 180 | °C | 260 | °C |
| Paverage reac | 40 | bar | 40 | bar |
| ρH2O (Treac,Preac) | 889 | kg/m3 | 787 | kg/m3 |
| ρPDMS (Tamb) | 963 | kg/m3 | 963 | kg/m3 |
| µPDMS (Tamb) | 5.00×104 | µPa.s | 5.00×104 | µPa.s |
| ρPDMS (Treac) | 818.717 | kg/m3 | 745.197 | kg/m3 |
| H2O pump | 0.09 | mL/min | 0.09 | ml/min |
| PDMS pump | 0.09 | mL/min | 0.09 | ml/min |
| H2O pump | 1.5×10-9 | m3/s | 1.5×10-9 | m3/s |
| PDMS pump | 1.5×10-9 | m3/s | 1.5×10-9 | m3/s |
| Residence time, Δt | 4.88 | s | 4.57 | s |
| Plug velocity, v | 4.51 ×10-2 | m/s | 4.82 × 10-2 | m/s |

These results revealed that the hydrodynamic conditions will depend on the range of mass flows that control the residence time of reactants in the heated section and ultimately the chemical reactions.

**Table S4. Experimental parameters**

|  |  |  |  |
| --- | --- | --- | --- |
| ID capillary | 0,0003 | 0,0003 | m |
| Radius of capillary | 0,00015 | 0,00015 | m |
| Section | 7,06858E-08 | 7,06858E-08 | m2 |
| Length | 0,22 | 0,22 | m |
| Residence time, Δt | 5 | 80 | s |
| Plug velocity, v | 0,044 | 0,00275 | m/s |
| Total pump | 0,186610604 | 0,011663163 | mL/min |
| Total pump | 3,11018E-09 | 1,94386E-10 | m3/s |
| Volume fed | 1,55509E-08 | 1,55509E-08 | m3 |
| Volume fed | 0,015550884 | 0,015550884 | mL |
| Volumetric flow rate of H2O pump | 0,093305302 | 0,005831581 | mL/min |
| Volumetric flow rate of PDMS pump | 0,093305302 | 0,005831581 | mL/min |
| ρH2O (Tamb,12bar) | 1000 | 1000 | kg/m3 |
| ρH2O (Tamb,70bar) | 1000 | 1000 | kg/m3 |
| µH2O(Tamb) | 0,0010005 | 0,0010005 | kg/ms |
| PH2O | 45,5 | 36,6 | bar |
| PPDMS | 56,3 | 37,3 | bar |
| Pressure drop, ΔPH2O pump to reactor | 1,26 | 0,41 | bar |
| Pressure drop, ΔPPDMS pump to reactor | 12,1 | 2,2 | bar |
| Collection amount | 0,5 | 0,5 | mL |
| Collection time | 5,358752293 | 85,74003668 | min |
| P reactor inlet | 44,24 | 36,19 | bar |
| P reactor inlet | 44,2 | 35,1 | bar |
| P inlet average | 44,22 | 35,645 | bar |
| P back pressure pump | 35 | 35 | bar |

# S7. Arrhenius plots

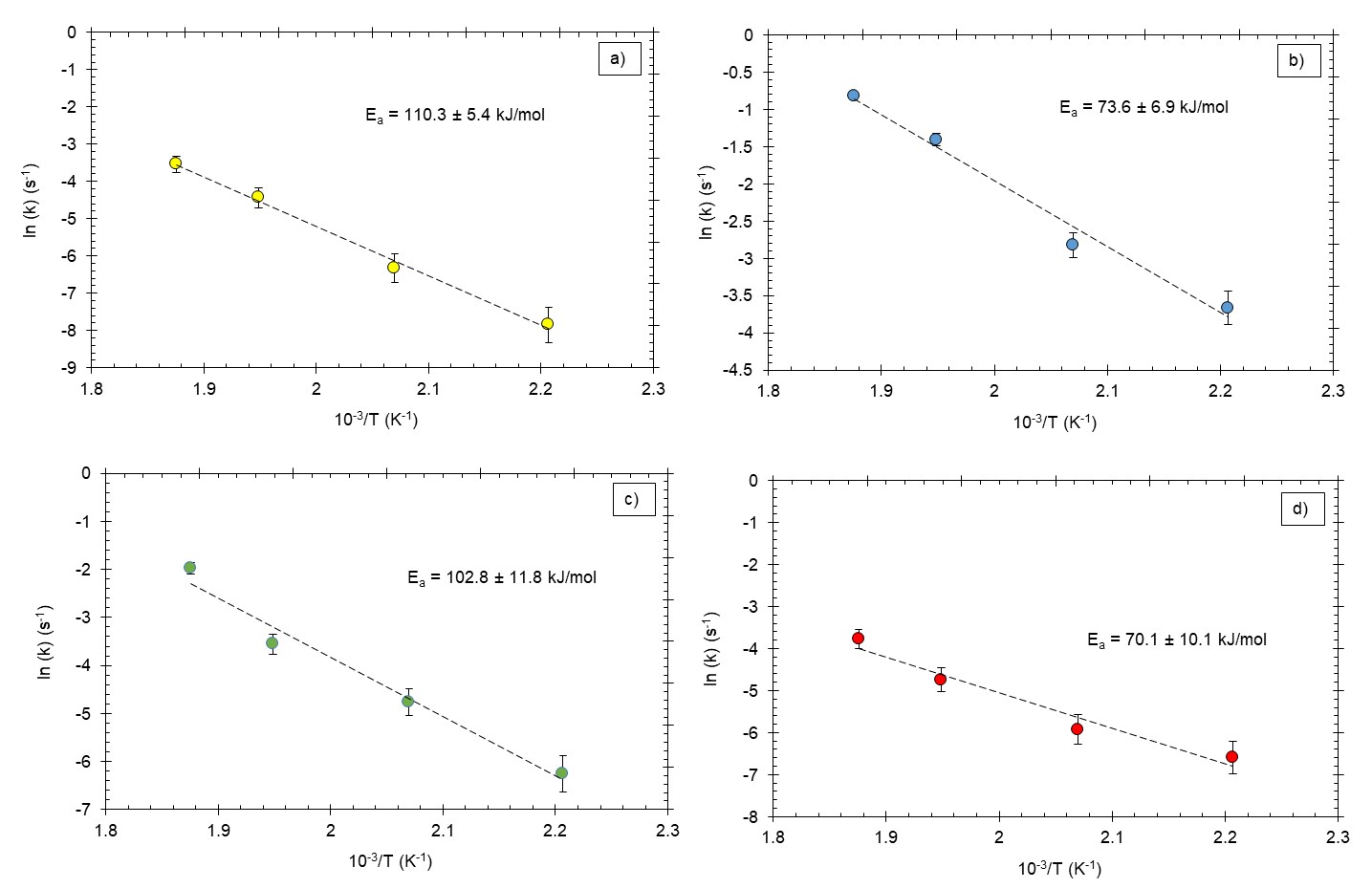


Figure S7. Arrhenius plots of a) glucose decomposition and product formation rates of b) fructose, c) levoglucosan and d) 5-HMF in the microfluidic reactor at temperatures of 180-260°C and residence times of 5-80 s.

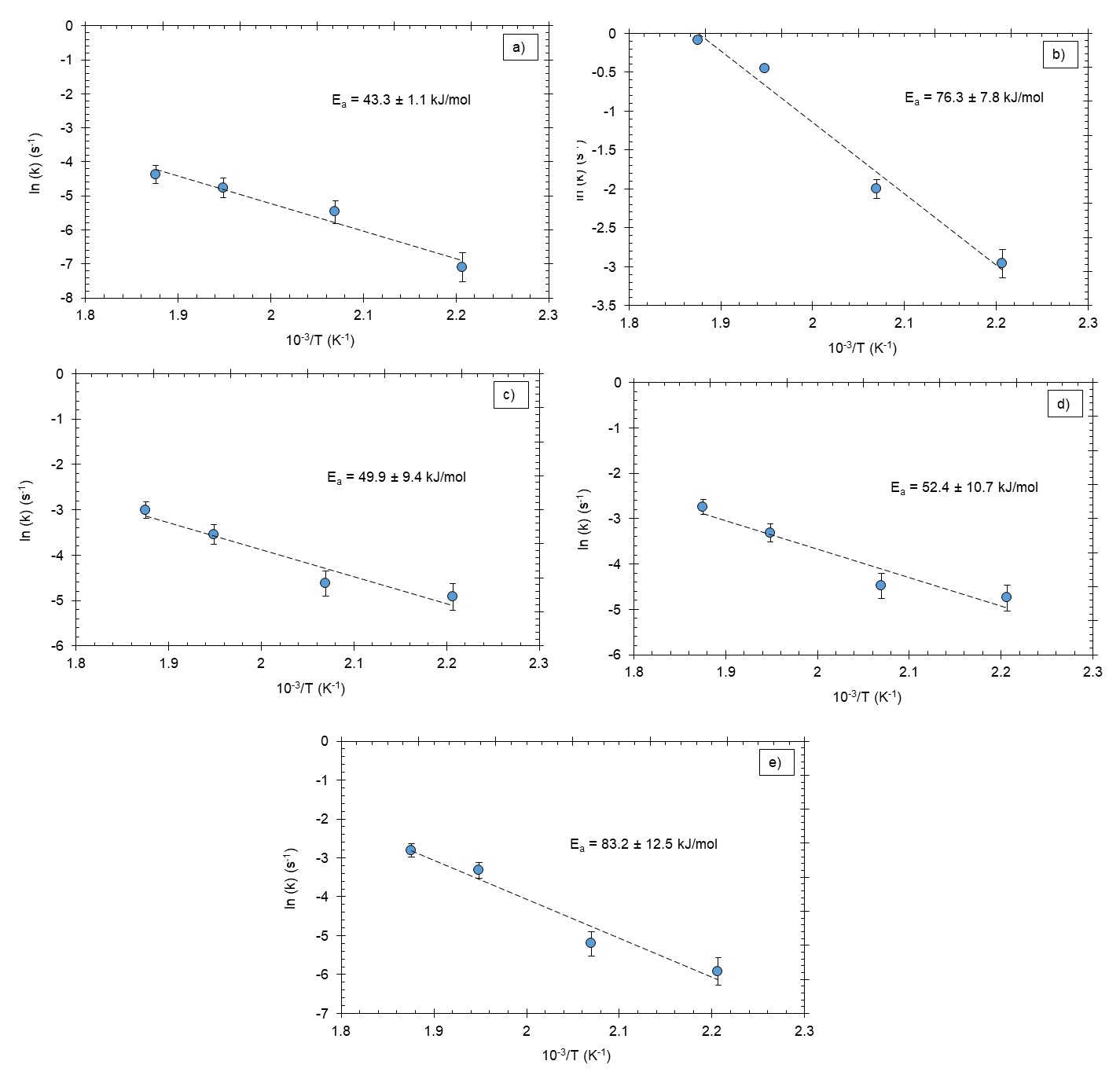


Figure S8. Arrhenius plot of a) the decomposition rate of cellobiose and the product formation rates of b) glucose, c) fructose, d) levoglucosan and e) 5-HMF in the microfluidic reactor at temperatures of 180-260°C and residence times of 10-80 s.