Supplementary Information

1. Estimation of reactor pressure

The pressure was calculated based on the assumption that all of the solvent was converted into supercritical fluid. The associated compressibility factor at the reduced temperature was 0.4 based on Lee Kesler's chart[1] for all the solvents except for GVL. Actual critical point data for GVL was not available in literature. Since gamma- butyrolactone or GBL, a chemically similar solvent to GVL has a critical temperature higher than 350 °C, it was assumed that GVL might also not be converted into supercritical fluid completely at this temperature. The compressibility factor for GVL was thus taken as 0.2. The following equation was used to determine the reactor pressure for each solvent system.

$$P = Z\frac{nRT}{V} \qquad \ldots (1)$$

Where

Z = compressibility factor for the fluid

n = moles of solvent

V = total volume of reactor = 2.5 mL

Solvent volume = 1.2 mL

2. Effect of temperature and pressure on solubility parameters[2]

Total solubility parameter or Hansen solubility parameter (δ_{Tot}) is based on the total energy of vaporization of a liquid that consists of several individual parts. These contributions arise from (atomic) dispersion forces, (molecular) permanent dipole–permanent dipole forces, and (molecular) hydrogen bonding (electron exchange). The three interaction forces give rise to each of the three individual parameters of the total solubility parameter. These constituent interaction parameters are known as dispersive solubility parameter (δ_D), polar solubility parameter (δ_P) and the hydrogen bonding solubility parameter (δ_H). Hansen total solubility parameter is related with its constituent parameter in the following way:

$$_{Tot} = \sqrt{(_D)^{2} + (_P)^{2} + (_H)^{2}}\ \delta\ \delta\ \delta\ \delta \qquad \dots (2)$$

Temperature and pressure can influence the total solubility parameter of the solvent. Temperature increase results in decrease in the solubility parameter whereas increase in pressure increases the solubility parameter due to increase in solvent density. Each term under the square root in the above equation changes with change in temperature and pressure. The individual relationship of these term with temperature and pressure are given below:

$$\delta_D = \frac{\delta_{Dref}}{\left(\frac{v_{ref}}{v}\right)^{-1.25}} \qquad \dots (3)$$

$$\delta_P = \frac{\delta_{Pref}}{\left(\frac{v_{ref}}{v}\right)^{-0.5}} \qquad \dots (4)$$

$$\delta_H = \frac{\delta_{Href}}{exp\left(-1.32 \times 10^{-3}\left(T_{ref} - T\right) - ln\left(\frac{v_{ref}}{v}\right)^{0.5}\right)} \qquad \dots (5)$$

$$\left(\frac{v_{ref}}{v}\right) = \frac{\rho}{\rho_{ref}} \qquad \dots (6)$$

$$\frac{\rho}{\rho_{ref}} = \frac{\rho}{\rho'} \times \frac{\rho'}{\rho_{ref}} \qquad \dots (7)$$

$$ln\frac{\rho'}{\rho_{ref}} = -\alpha(T - T_{ref}) \qquad \dots (8)$$

$$ln\frac{\rho}{\rho'} = \beta(P - P_{ref}) \qquad \dots (9)$$

Where

δ_{Dref}, δ_{Pref}, δ_{Href} = the values of dispersion parameter, polar interaction parameter and hydrogen bonding parameter at T_{ref} and P_{ref} .

v_{ref} and v = molar volumes of the solvent at T_{ref} and P_{ref} and the reaction temperature and pressure, respectively.

ρ_{ref}, ρ' and ρ = solvent densities at T_{ref} and P_{ref}, T and P_{ref}, T and P respectively.

α = cubic expansion coefficient of solvent at 25 °C and 1 atm.

β = isothermal compressibility of solvent at 25 °C and 1 atm.

T_{ref} and T = 25 °C and reaction temperature, respectively.

P_{ref} and P = 1 atm and reaction pressure, respectively.

3. Activation energy of cellulose solvolysis

Activation energies of cellulose degradation in different solvents were obtained using Arrhenius plots of the solvolysis rate constants at three different temperatures in the range of 325 to 375 °C. This study was performed in THF, acetonitrile and GVL systems with 20 mg cellulose as initial substrate. The solvolysis rate constant at a certain temperature was calculated based on a first order assumption for the initial rate of cellulose decomposition reaction. The details of the activation energy calculation procedure are provided below and the related plots are shown in Figures S1-S3.

Cellulose degradation in the aprotic solvents was modeled as a first order reaction and the reaction rate constant at each temperature was determined based on the initial slope of the cellulose residue versus time plot. Arrhenius principle was used to calculate the slope of ln K versus T^{-1} plot for each solvent system and subsequently the activation energy was determined from the slope.

$$-\frac{dC}{dt} = KC \qquad \ldots (10)$$

Where

C = unreacted cellulose residue at time, t and K is the rate constant.

Arrhenius law describes the relation between K and the reaction temperature T:

$$\ln K = \left(-\frac{E_{app}}{R}\right)\frac{1}{T} + \ln A \qquad \ldots (11)$$

Where

E_{app} = apparent activation energy in J mol^{-1}

A = the frequency factor

4. Tables

Table **S1**. Boiling points and critical points of the polar aprotic solvents[3, 4]

Solvent	**Boiling point (^{o}C)**	**Critical point**
1,4-dioxane	101	314 ^{o}C and 5.21 MPa
Ethyl acetate	77	260 ^{o}C and 3.90 MPa
THF	66	268 ^{o}C and 5.19 MPa
MIBK	116	298 ^{o}C and 3.27 MPa
Acetone	56	235 ^{o}C and 4.80 MPa
Acetonitrile	82	272 ^{o}C and 4.87 MPa
GVL	207-208	Not available

Table **S2**. Estimated pressure inside the reactors at 350 ^{o}C

Solvent	**Pressure (MPa)**
1,4-dioxane	12
Ethyl acetate	10
THF	12
MIBK	8
Acetone	13
Acetonitrile	19
GVL	5

Table **S3**. Solubility parameters of the polar aprotic solvents at T_{ref} and P_{ref} (25 ^{o}C and 1 atm)[2]

Solvent	δ_{Dref} **(MPa$^{1/2}$)**	δ_{Pref} **(MPa$^{1/2}$)**	δ_{Href} **(MPa$^{1/2}$)**	δ_{ref} **(MPa$^{1/2}$)**
1,4-dioxane	17.5	1.80	9.0	19.8
Ethyl acetate	15.8	5.30	7.2	18.2
THF	16.8	5.70	8.0	19.5
MIBK	15.3	6.10	4.1	17.0
Acetone	15.5	10.4	7.0	20.0
Acetonitrile	15.3	18.0	6.1	24.4
GVL (approximated) [a]	19.0	16.6	7.4	26.3

a: Since contribution of a methyl group to three individual interaction parameter in a cyclic compound can assumed to be negligible, individual and total solubility parameters for GVL were approximated as that of gamma-butyrolactone or GBL due to unavailability of actual data for GVL.[2]

Table **S4**. Thermophysical properties of polar aprotic solvents[4-10]

Solvent	α **(K^{-1})**	β **(MPa^{-1})**	ρ_{ref} **(g cm^{-3})**	ρ **(g cm^{-3})**
1,4-dioxane	0.00106	0.000749	1.034	0.738
Ethyl acetate	0.00135	0.001132	0.901	0.583
THF	0.00126	0.000800	0.889	0.594
MIBK	0.00120	0.001100	0.800	0.544
Acetone	0.00146	0.001262	0.790	0.497
Acetonitrile	0.00133	0.001070	0.782	0.521
GVL (approximated) [b]	0.00074	0.000400	1.057	0.824

b: approximated by the thermophysical properties of GBL to maintain consistency with Table S3 estimation procedure.

Table **S5**. Solubility parameters of the polar aprotic solvents at reaction temperature and pressure

Solvent	δ_D **(MPa$^{1/2}$)**	δ_P **(MPa$^{1/2}$)**	δ_H **(MPa$^{1/2}$)**	δ_{Tot} **(MPa$^{1/2}$)**
1,4-dioxane	26.6	2.10	0.5	26.7
Ethyl acetate	27.0	6.60	0.4	27.7
THF	27.7	7.00	0.4	28.6
MIBK	24.6	7.40	0.2	25.7
Acetone	27.5	13.1	0.4	30.4
Acetonitrile	25.6	22.1	0.3	33.8
GVL	25.6	18.7	0.4	31.7

Table **S6**. Apparent activation energy of cellulose solvolysis in different solvents[c]

Solvent	**E_{app} (kcal mol^{-1})**
THF	26.53
GVL	19.70
Acetonitrile	20.23

c: calculation of rate constant at each temperature for Arrhenius plot was done considering the initial rate of cellulose conversion with first order assumption. Initial feedstock was 20 mg cellulose.

5. Figures

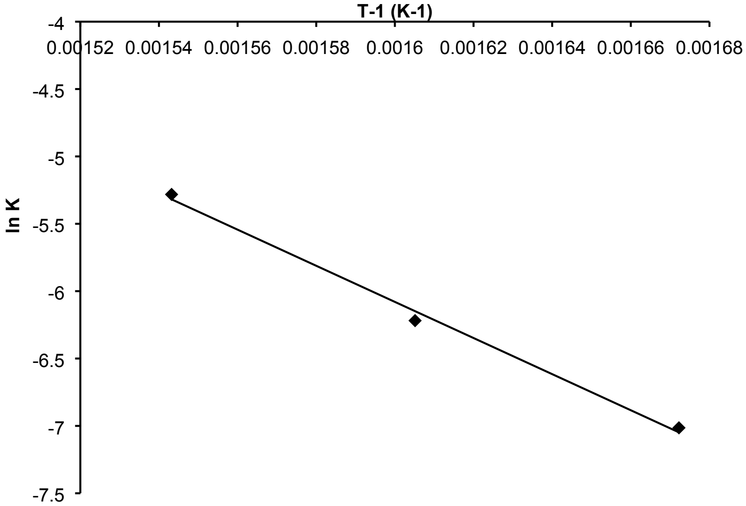

Figure S1. Arrhenius plot for THF solvent system

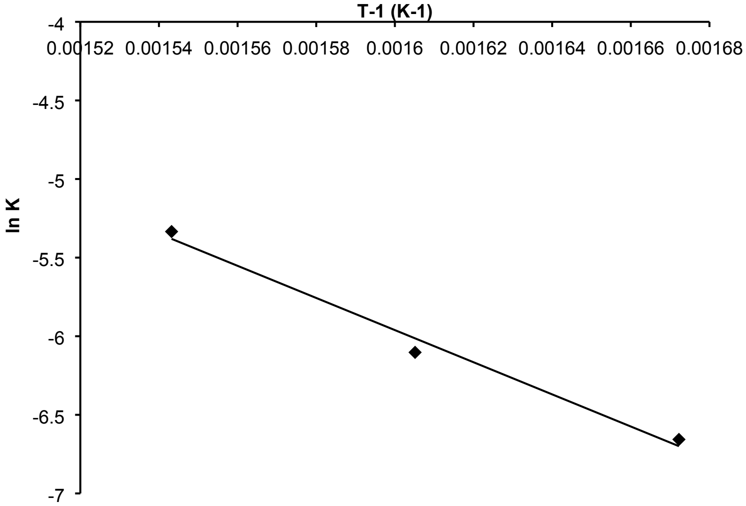

Figure S2. Arrhenius plot for acetonitrile solvent system

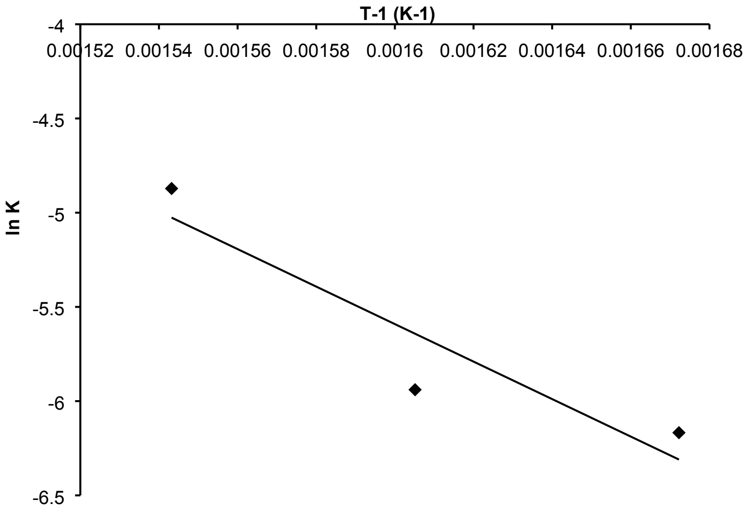

Figure S3. Arrhenius plot for GVL solvent system

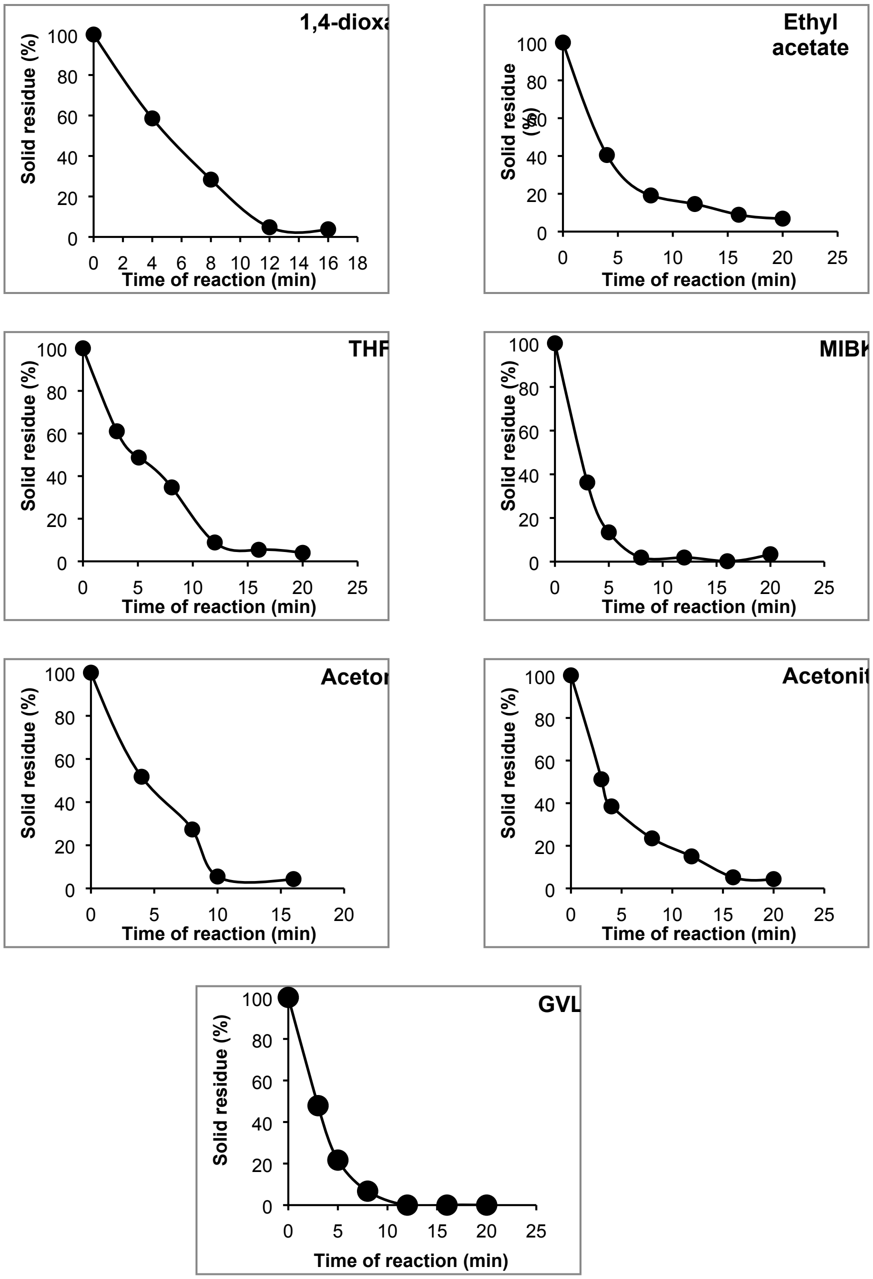

Figure S4. Solid residue with increasing time of reaction at 350 °C with 20 mg cellulose in different solvent systems.

References

1. B. I. Lee and M. G. Kesler, *Aiche J*, 1975, **21**, 510-527.
2. C. M. Hansen, *Hansen solubility parameters: a user's handbook*, CRC press, 2012.
3. G. A. Burdock, *Fenaroli's handbook of flavor ingredients*, CRC press, 2009.
4. W. M. Haynes, *CRC handbook of chemistry and physics*, CRC press, 2013.
5. Antonenk.Ti and V. I. Rykov, *Izv Vuz Fiz+*, 1968, 80-&.
6. U. Domańska, J. Łachwa and T. M. Letcher, *Journal of Chemical & Engineering Data*, 2002, **47**, 1446-1452.
7. D. R. Lide and H. V. Kehiaian, *CRC handbook of thermophysical and thermochemical data*, CRC Press, 1994.
8. H. Piekarski, K. Kubalczyk and M. Wasiak, *J Chem Eng Data*, 2010, **55**, 5435-5440.
9. J. A. Riddick, W. B. Bunger and T. K. Sakano, 1986.
10. M. N. Rodnikova, V. M. Troitskii, D. B. Kayumova, I. A. Solonina and M. A. Gunina, *Russ J Phys Chem a+*, 2010, **84**, 2190-2192.

Web based resources used

(a) NIST Chemistry WebBook, http://webbook.nist.gov/chemistry/, (accessed April 2015)

(b) Tetrahydrofuran physical data and properties,

http://terathane.invista.com/doc/files/781/thf_data_sheet.pdf, (accessed April 2015)

(c) MIBK thermophysical properties, http://www.coralenergy.gr/media/ximika/TDS_MIBK.pdf,

(accessed April 2015)

(d) Acetonitrile and GBL thermophysical properties, http://virtualchemistry.org/molecules,

(accessed April 2015)