Breaking the Equilibrium at the Interface: Microwave-Assisted Reactive Distillation (MARD)

Electronic Supplementary Information (ESI)

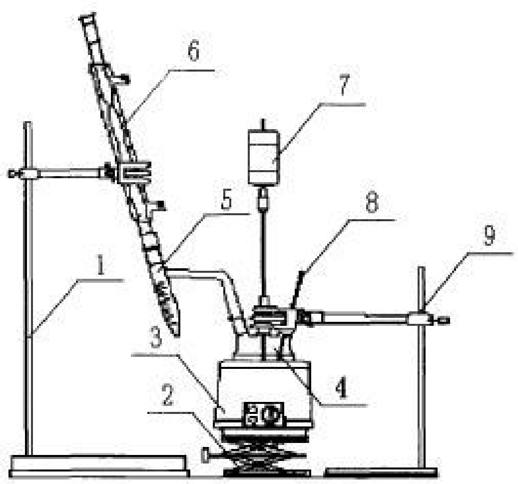

Fig. S1. Experimental rig for reactive distillation by conventional heating. 1 and 9. Lab stand supports, 2. Lifting platform, 3. Heating mantle, 4. Three-necked flask, 5. Oil-water separator, 6. Spherical condenser, 7. Overhead stirrer, 8. Thermometer and sampler.

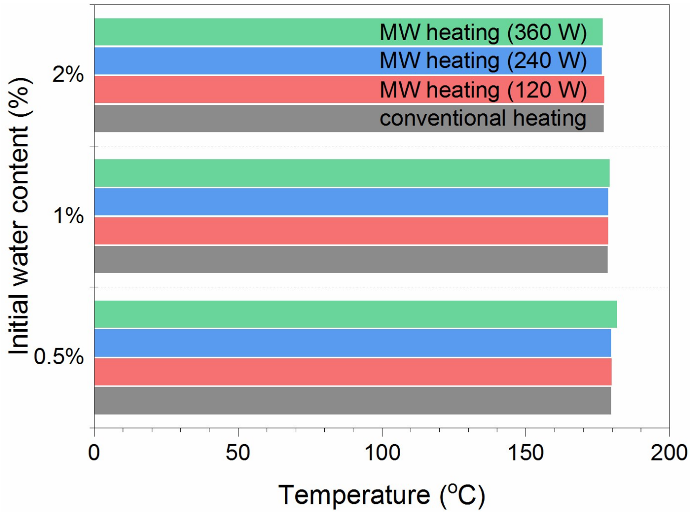

Fig. S2. Measured temperatures of 2-ethylhexanol/water binary systems at the gas-liquid phase equilibria under the conventional and microwave heating.

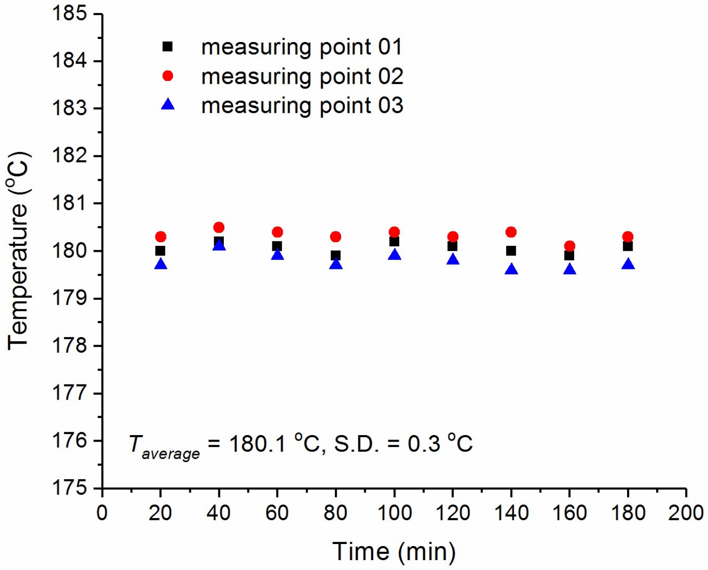

Fig. S3. Temperature as a function of time at three different measuring points in the microwave heating system.

Kinetic modelling:

Since the formation of the monoester is fast, the assumption was made to consider the Step one reaction (Scheme 1) insignificant regarding the kinetics of the system. Therefore, the rate of the reaction can be approximated by the first-order rate law in Eq. S1.

$$r = {}^{dC_M}\!/_{dt} = kC_M^tC_A^t \tag{S1}$$

where C_M^t and C_A^t are the molar concentration of the monoester and isooctyl alcohol (mol/l), respectively, at time t, and k is the forward reaction rate constant (l/mol·min).

The conversion of the monoester (η) is described by Eq. S2.

$$\eta = \frac{n_M^0 - n_M^t}{n_M^0} = \frac{C_M^0 - C_M^t}{C_M^0} \tag{S2}$$

where n_M^0 is the initial molar quantity of monoester (mol); n_M^t is the molar quantity of monoester at time t (mol); C_M^0 is the initial molar concentration of monoester (mol/l).

The molar concentration of isooctyl alcohol during the reaction can be represented by the conversion and the initial molar concentration of isooctyl alcohol and monoester, as in Eq. S3.

$$C_A^t = C_A^0 - C_M^0 \cdot \eta = C_M^0(\alpha - \eta) \tag{S3}$$

where α is the initial molar concentration ratio between isooctyl alcohol and monoester, defined by Eq. 4.

$$\alpha = {}^{C_A^0}\!/_{C_M^0} \tag{S4}$$

Therefore, Eq. 5 can be achieved as:

$$k \cdot C_M^0 \cdot dt = \frac{d\eta}{(1-\eta)(\alpha-\eta)} \tag{S5}$$

This equation can then be integrated, giving the following Eq. S6.

$$k \cdot t = \frac{\left(\frac{1}{\alpha-1}\right)\ln\left(\frac{\alpha-\eta}{1-\eta}\right) - \left(\frac{1}{\alpha-1}\right)\ln\alpha}{C_M^0} = Z \tag{S6}$$

Accordingly, if the *Z* in Eq. S6 is linearly related with time *t*, the rate equation of Eq. S1, representing the DOP esterification reaction, should be valid. By interpreting the kinetic data using Eq. S6, the corresponding parameters of DOP synthesis (*i.e.* the rate constant, *k*) can be obtained using the nonlinear least-squares method. *Z*-*t* plots for various systems at different temperatures under conventional heating and microwave irradiation are presented in Fig. S3, Therefore, the rate constants at various temperature were extracted and subsequently used for estimating the apparent activation energy of the systems.

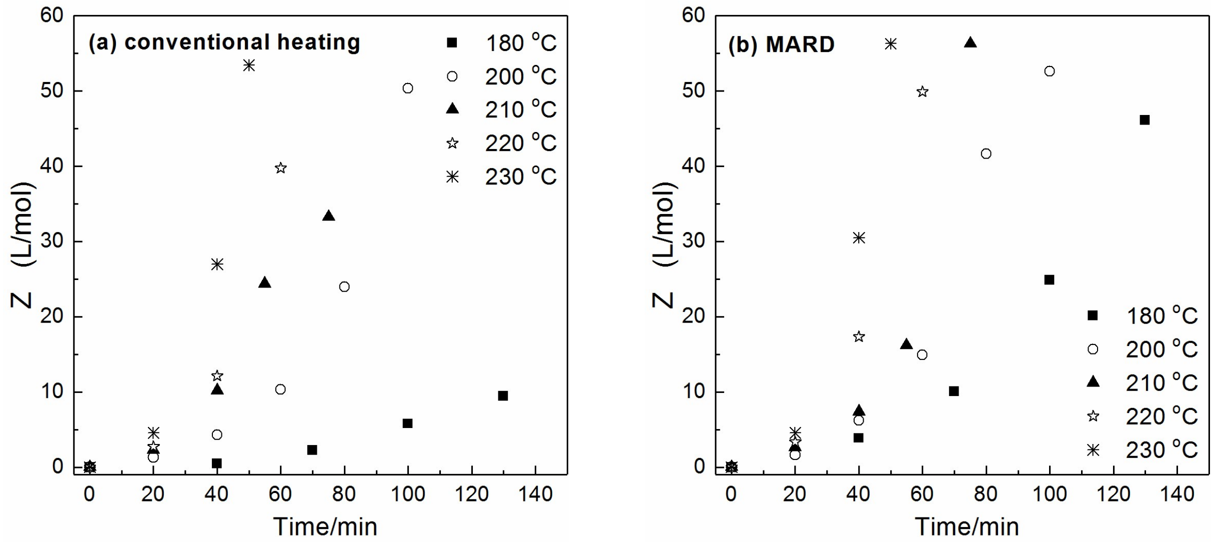

Fig. 4 *Z*-*t* plots for the synthesis of DOP by (a) conventional heating and (b) microwave irradiation.

According to the Arrhenius law, the linear correlation of ln*k* with 1/*T* (Eq. S7) can be used to estimate the activation energy of the reaction DOP esterification reaction can be determined using the kinetic constants at different temperatures. Therefore, the pre-exponential factor *A* and activation energy *E* (J/mol) can be calculated:

$$\ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} \tag{S7}$$

where *A* is the pre-exponential factor (l/mol·min), E_a is the activation energy (J/mol) and *R* is the gas constant (8.314 J/mol·K).

Nomenclature

A	pre-exponential factors,	l/mol·min
C_A^0	initial molar quantity of isooctyl alcohol,	mol
C_M^0	initial molar concentration of monoester,	mol/l
C_A	molar concentration of isooctyl alcohol,	mol/l
C_M	molar concentration of monoester,	mol/l
E	activation energies,	J/mol
k	forward rate constant,	l/mol·min
n_M^0	initial molar quantity of monoester,	mol
n_M	molar quantity of monoester at one time,	mol
r	reaction rate,	mol/l·min
R	molar gas constant,	J/mol·K
R^2	correlation coefficient,	-
t	reaction time,	min
T	reaction temperature,	K
Greek letters		
α	initial molar concentration ratio	-
η	reaction conversion	-