

# Effect of moisture content on curing kinetics of pMDI resin and wood mixtures

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## Abstract

The curing process of polymeric diphenylmethane diisocyanate (pMDI) with wood is affected significantly by moisture in the wood since the reaction of isocyanate is highly sensitive to water. This study determined the curing kinetics of pMDI and wood mixtures containing various moisture contents by means of differential scanning calorimetry (DSC). Model-free analysis of the kinetics suggested that the curing reactions for the oven-dried wood/pMDI mixture are different from those of the mixtures with moisture. Peak temperatures indicated that the activation energy, reaction enthalpy, and reaction rate were lower for the oven-dried wood and resin mixture because the curing process was controlled by diffusion in the absence of moisture. The activation energy increased when moisture was present, but decreased when the moisture content further increased. Both the reaction enthalpy and reaction rate increased with the increase in moisture content and remained almost unchanged or increased slightly after the moisture content reached 12%.

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## 1. Introduction

The use of polymeric diphenylmethane diisocyanate (pMDI) resin as a thermosetting adhesive for wood-based composites has been steadily increasing over the past decade. Compared to conventional wood adhesives, pMDI has some unique characteristics, such as fast curing rate, formaldehyde emission-free, good weather resistance, and small loading quantity. Isocyanate chemistry has revealed that multiple reactions exist for the formation of isocyanate/wood bonds [1–8]. The hydroxyl groups in wood may react with isocyanate to form polyurethane, providing direct covalent linkages between the adhesive and wood. However, the reaction of isocyanate with water absorbed in wood to form polyurea and biuret-type structures can compete strongly with the urethane formation.

There is some controversy on the various reactions during pMDI adhesive bonding with wood. Fourier transform infrared spectroscopy analysis indicated that urethane bonds could be formed under anhydrous conditions when an excess of isocyanate was used [3,7]. Other studies revealed that the reactions of pMDI with water to form polyurea were dominant when moisture was present [3,8]. Studies [4,5] on pMDI/wood bondline by nuclear magnetic resonance spectroscopy gave the results that the curing chemistry of pMDI with dried wood resulted primarily in biuret-type structures from the isocyanate reaction with a small amount of moisture. When the precure moisture content of wood was increased to 4.5%, the end products of curing were primarily polyurea-type structures with less biuret formation and residual isocyanate. The urethane formation could not be detected by this technique unless it was present in very significant amounts, because the resonance peak for urethane overlapped with the resonance peak for urea. Furthermore, the thermal

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decomposition of biuret may liberate isocyanate, which can react with the hydroxyl groups in wood to form urethane as curing time increases at elevated temperature [4].

Kinetic studies may shed some light on reaction characteristics or verify reaction mechanisms. However, little research has been done on the kinetics of wood/isocyanate reactions [9–11]. To obtain information on wood/isocyanate reaction characteristics, the kinetics of wood/isocyanate reactions under different moisture contents were determined by differential scanning calorimetry (DSC). The variation in kinetic parameters was used to interpret the reaction characteristics of wood/isocyanate on the basis of isocyanate chemistry.

## 2. Experimental

### 2.1. Sample preparation

Polymeric methylene diphenyl diisocyanate (pMDI) resin was supplied by Huntsman Polyurethanes (Geismar, LA, USA). Aspen (*Populus tremuloides*) was used as a wood reactant in this research. Wood was first ground into flour. The wood flour was then screened, and wood flour between 35 and 60 mesh was retained for the experiments. The flour was either conditioned to the target moisture content (MC) of 6% and 12% or dried in the oven at 103 °C for 24 h to obtain oven-dried wood. The wood flour with a moisture content of 50% was obtained by mixing oven-dried flour with distilled water at a 50/50 mass ratio. The resin/wood mixtures were prepared by mixing the pMDI resin with the wood flour (including moisture) at a 50/50 mass ratio for all experiments.

### 2.2. Differential scanning calorimetry (DSC) measurements

All DSC measurements and analyses were made using a Q1000 DSC and the Universal analysis software from TA instruments. High-volume pans that can withstand vapor pressure up to 3.8 MPa were used to prevent components of the test samples from evaporating at higher temperatures up to 250 °C. Dynamic scans were made at heating rates of 2, 5 and 10 °C/min, and the samples were scanned from 25 to 250 °C. Two replicates were done for each scan. The maximum variability was 1.0 °C for peak temperature and 5% for reaction enthalpy.

## 3. Results and discussion

### 3.1. DSC kinetic evaluation

The activation energy of the curing process was evaluated by isoconversional methods using peak

temperatures of the DSC scans at three different heating rates. These methods utilize the relationship between the heating rate and temperature at the peak of the DSC curve or at a given degree of conversion. Based on the work of Ozawa [12] and Flynn and Wall [13] an equation connecting heating rate and temperature can be obtained by assuming that  $A$ ,  $E_a$  and  $f(\alpha)$  are independent of temperature and heating rate, as given below:

$$\log \Phi = -2.315 - 0.4567 \frac{E_a}{RT} + \log \left( \frac{AE_a}{R} \right) - \log F(\alpha), \quad (1)$$

where  $F(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$ ,  $\alpha$  is the degree of conversion,  $f(\alpha)$  is a function of  $\alpha$ ,  $\Phi$  is the heating rate,  $T$  is the temperature,  $E_a$  is the apparent activation energy,  $A$  is the pre-exponential factor and  $R$  is the gas constant. The activation energy was calculated from the plot of  $\log \Phi$  versus  $1/T$ . Another expression relating the heating rate and temperature was developed by Kissinger [14] for the  $n$ th-order reaction as follows:

$$\ln \left( \frac{\Phi}{T^2} \right) = \frac{E_a}{RT} + \ln \left( \frac{RA}{E_a} \right). \quad (2)$$

A plot of  $\ln(\Phi/T^2)$  versus  $1/T$  is a straight line, from which the activation energy and the pre-exponential factor can be obtained respectively.

A modified pre-exponential factor for autocatalyzed kinetics has been also introduced by Prime [15] as shown in the following:

$$A \cong \frac{\Phi E_a \exp(E_a/(RT_p))}{RT_p^2(2\alpha_p + 2B\alpha_p - 3\alpha_p^2 - B)}, \quad (3)$$

where  $B$  is the stoichiometric ratio of reactants,  $\alpha_p$  is the degree of conversion at the peak, and  $T_p$  is the peak temperature. Assuming  $\mu$  represents  $2\alpha_p + 2B\alpha_p - 3\alpha_p^2 - B$ , the equation for kinetics of an autocatalyzed reaction is obtained from Eq. (3) as

$$\ln \left( \frac{\Phi}{\mu T^2} \right) = \frac{E_a}{RT} + \ln \left( \frac{RA}{E_a} \right). \quad (4)$$

The reaction rate constant,  $k$ , at a given temperature can be calculated by the Arrhenius equation

$$k = A \exp \left( \frac{E_a}{RT} \right). \quad (5)$$

A prediction of isothermal kinetic parameter can be done using nonisothermal DSC data obtained above. The reaction time to reach a given degree of conversion at an arbitrary temperature can be calculated by introducing an integrated equation as follows [16,17]

$$t_\alpha = \left[ \Phi \exp \left( -\frac{E_{a,\alpha}}{RT_{iso}} \right) \right]^{-1} \int_{T_0}^{T_\alpha} \exp \left( -\frac{E_{a,\alpha}}{RT} \right) dT, \quad (6)$$

where  $t_\alpha$  is the reaction time to reach the degree of conversion,  $\alpha$ , at the isothermal temperature ( $T_{\text{iso}}$ );  $E_{a,\alpha}$  is the activation energy at the degree of conversion,  $\alpha$ ;  $T_0$ , and  $T_\alpha$  are the scanning temperatures at the degree of conversion 0 and  $\alpha$ , respectively.

### 3.2. Kinetic analysis of pMDI/wood reactions

Based on the chemistry of isocyanates [18] the main reactions of pMDI with wood in the presence of moisture may include primary and secondary reactions. First, isocyanate reacts with primary and secondary hydroxyls in the wood to form urethane and with water absorbed in the wood to form urea. Urethane and urea then react with isocyanate, as the secondary reactions, to form allophanate and biuret, respectively. It should be noted that the secondary reactions mentioned above are thermally reversible. These primary and secondary reactions are the main factors that affect kinetics in the curing of pMDI/wood mixtures with different moisture contents.

The DSC scanning curves for the pMDI/wood mixtures with different moisture contents are shown in Fig. 1. The curves each showed a single peak for all moisture contents, but the peak was shifted to lower temperatures when the moisture content was increased. It was also found that the peak became sharper when

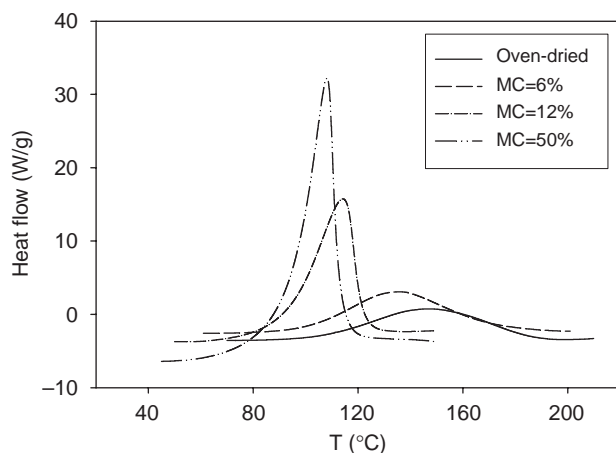


Fig. 1. DSC scanning curves for the curing process of the pMDI/wood mixtures (heating rate: 5 °C/min).

moisture content of the mixture was increased, especially when moisture contents were 12% and 50%.

Table 1 lists the peak temperatures and calculated activation energy based on the peak temperatures for the pMDI/wood mixtures. Since the kinetics of pMDI/wood reactions displayed evidence of autocatalysis [11] and the Kissinger method was developed for the  $n$ th-order kinetics, it was interesting to see that the activation energies ( $E_a^{\text{Ki}}$ ) calculated by the Kissinger method were comparable to the results ( $E_a^{\text{Oz}}$ ) by the Ozawa method and the corresponding coefficient was high. The values of  $E_a^{\text{Ki}}$  were generally about 3 kJ/mol less than those of  $E_a^{\text{Oz}}$  for all the samples studied.

It should be noted that the isocyanate/wood reaction is known to have autocatalyzed features [11], although the Kissinger method could be used to calculate the kinetic parameters. It was necessary to calculate the activation energy ( $E_a$ ) using the autocatalyzed kinetics. Assuming  $B = 1$  for all mixed samples, the activation energies ( $E_a$ ) calculated using the autocatalyzed kinetics are shown in Table 2. It was found that the values of  $E_a$  were close to the values of  $E_a^{\text{Ki}}$  except for the oven-dried wood mixture. The probable reason for the deviation was that the assumption for the stoichiometric ratio,  $B$ , did not represent the actual situation. For the oven-dried wood mixture, little water existed inside the wood and most of hydroxyls of wood (i.e., cellulose, hemicellulose and lignin), were restricted in terms of accessibility and reaction with the isocyanate molecules, resulting in a lower stoichiometric ratio. If a lower stoichiometric ratio,  $B = 0.5$ , was arbitrarily chosen for the oven-dried wood mixture, the corresponding activation energy was recalculated as 55.4 kJ/mol with the high coefficient of 1. This value was very close to the values of  $E_a^{\text{Ki}}$  and  $E_a^{\text{Oz}}$ . Therefore, it showed that a lower stoichiometric ratio was more suitable for the oven-dried wood mixture.

The relationship between the activation energy and moisture content seemed difficult to understand as illustrated in Fig. 2. It can be seen that the activation energy increased when the moisture content changed from 0% (oven-dried mixture) to 6%, and then decreased with the further increase in the moisture content. One possible explanation is that the dominant reaction between pMDI and the oven-dried wood was of

Table 1  
Peak temperature and activation energy of pMDI/wood

Samples	$T_p$ (°C)			$E_a^{\text{Ki}}$ (kJ/mol)	$R^2$	$E_a^{\text{Oz}}$ (kJ/mol)	$R^2$
	2 °C/min	5 °C/min	10 °C/min				
Oven-dried	126.3	146.8	164.5	54.3	0.9998	58.2	0.9999
MC = 6%	118.3	135.7	147.4	68.5	0.9971	71.5	0.9975
MC = 12%	100.4	114.3	128.5	65.1	0.9946	68.1	0.9957
MC = 50%	92.2	108.2	121.0	60.7	1	63.7	1

Table 2  
Peak conversion and activation energy by autocatalyzed kinetics  
( $B = 1$ )

Samples	$\alpha_p$ (%)			$E_a$ (kJ/mol)	$R^2$
	2 °C/min	5 °C/min	10 °C/min		
Oven-dried	48.0	51.5	55.3	44.6	0.9997
MC = 6%	47.9	49.2	48.6	66.7	0.9925
MC = 12%	73.5	70.3	65.1	63.3	0.9955
MC = 50%	74.5	68.4	61.5	59.2	0.9990

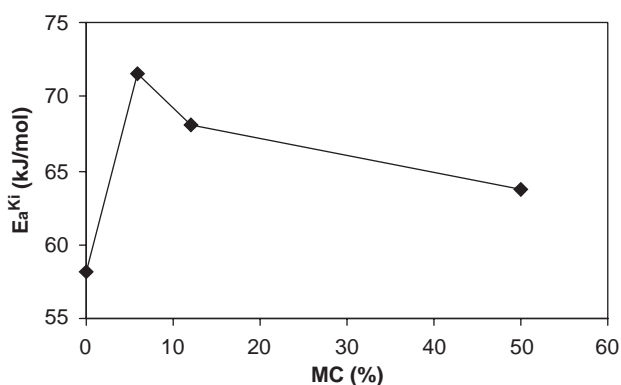


Fig. 2. Variation of activation energy with moisture content.

isocyanate with hydroxyl groups, while the dominant reaction between pMDI and the moist wood was of isocyanate with water. The difference in the activation energy between these two types of reactions could lead to the increase in the activation energy from the oven-dried mixture to the mixture with moisture. However, it cannot explain the decrease in the activation energy with the further increase in moisture content. In fact, the activation energy decreased with the increase in the moisture content, indicating that the pMDI/water reactions probably had a lower activation energy. Another explanation could be that the reactions of isocyanate with wood without moisture are diffusion-controlled, because the reactants of wood, including cellulose, hemi-cellulose and lignin, are macromolecules. Plus some cellulose regions are highly crystalline, resulting in a lower mobility of these reactants. The apparent activation energy will be influenced by the intrinsic activation energies for both chemical reaction and diffusion when the reaction is diffusion-controlled [16,17]. This can lead to a lower apparent activation energy because of the low activation energy for diffusion.

The variation in reaction rate constant with moisture content is shown in Fig. 3. The rate constant increased with the increase in moisture content. This trend suggested that water reacts with isocyanate faster than

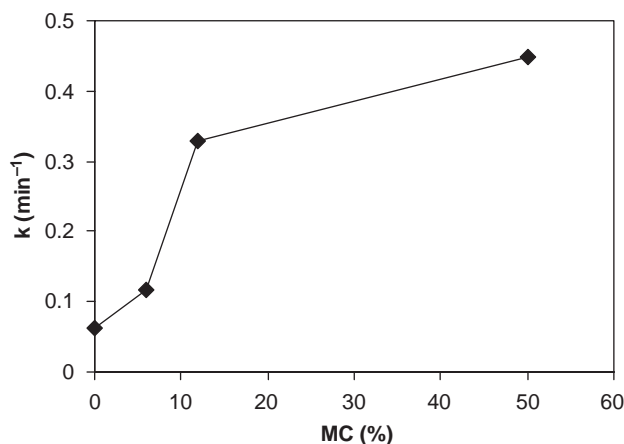


Fig. 3. Variation of reaction rate constant with moisture content.

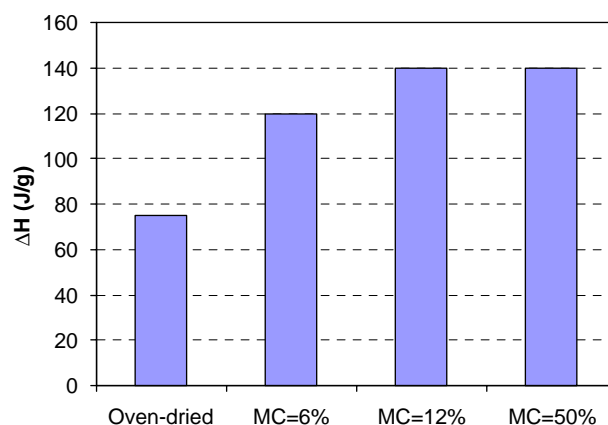


Fig. 4. Variation of reaction enthalpy with moisture content (reaction enthalpy is based on the weight of pMDI + wood + moisture).

wood alone does, since water has a much higher mobility than the hydroxyls in wood. It is interesting that the rate constant increased most when the moisture content of the mixture was increased from 6% to 12%. This indicated that the curing rate was very sensitive to the amount of water in the mixture in this moisture content range.

The reaction enthalpy generally increased with the increase in moisture content as illustrated in Fig. 4. It is evident that the increase mainly occurred between the oven-dried mixture and the mixture with 6% moisture content. This is reasonable because in the case of oven-dried wood mixture, there is very limited amount of water in wood that could react with the isocyanate, and most of the hydroxyls in wood are not able to react with the isocyanate due to the low mobility. This led to more isocyanate molecules remaining in the curing system and a lower reaction enthalpy. The reaction of isocyanate with water was dominant once the moisture is introduced into the wood, leading to a quick increase in the

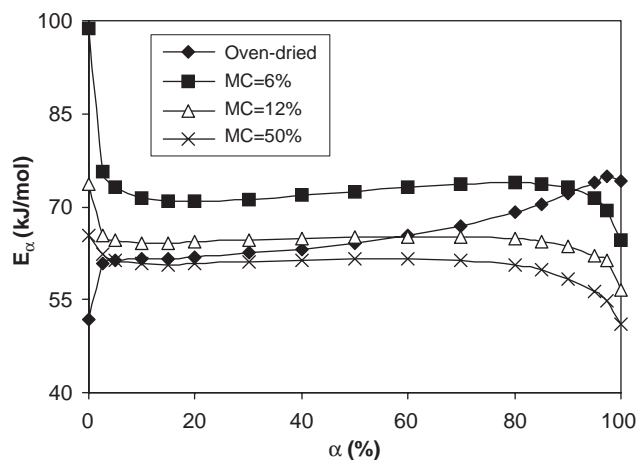


Fig. 5. Dependence of activation energy on the degree of conversion.

reaction enthalpy. The reaction enthalpy increased with the further increase in the moisture content, but the increase was moderate. The change in the reaction enthalpy was very small after the moisture content reached 12%.

It is known that the curing process of pMDI with wood containing moisture has several types of reactions, depending on the moisture content and reaction temperature. This complex process could not be entirely characterized using only the peak temperature. It was more useful to analyze the whole curing process using model-free kinetics [16,17], which describes the reaction kinetics using the dependence of the activation energy on the degree of conversion.

The dependence of the activation energy on the degree of conversion for the pMDI/wood mixture is shown in Fig. 5. In Fig. 5, the values for the activation energies at very low and very high degrees of cure were in general more variable since they are typically more sensitive to the baseline selection. However, we found in our experiments that the trend was the same for all repeated scans and replicate samples even at low and high degrees of cure. It is obvious that the relationship between the activation energy and the degree of conversion was different for the oven-dried mixture and the mixtures with moisture. These differences revealed that the curing process was influenced by the moisture present in wood.

For the oven-dried wood mixture, the activation energy increased with the degree of conversion at the beginning of the reaction, indicating that the parallel reactions occurred simultaneously [17]. The activation energy then remained almost constant and increased slightly as the reaction proceeded, but increased more quickly at the higher degrees of conversion. This trend was probably the result of the reaction of urea to form biuret and the decomposition of biuret to urea at the high temperature according to previous research [5]. The

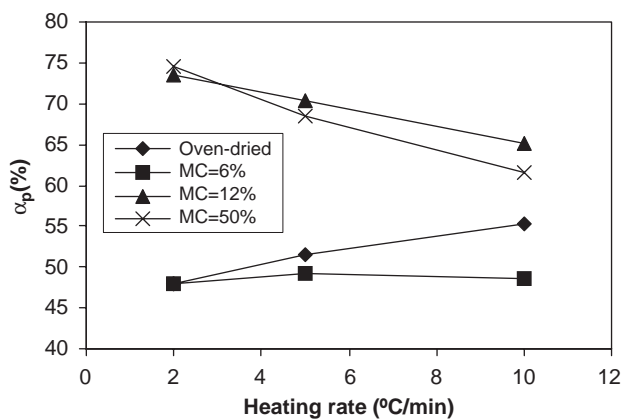


Fig. 6. Variation of peak conversion with the heating rate.

decomposition of biuret has a higher activation energy, and, therefore, gives a higher apparent activation energy.

The curing processes of the pMDI/wood mixtures became very different after moisture was introduced into the wood. At the beginning of the curing reactions, the activation energy decreased and the curve of the activation energy versus the degree of conversion had a concave shape, suggesting that the reaction displayed an autocatalyzed kinetic feature [16]. The activation energy was then remained constant, indicating that the individual reactions were relatively stable as the degree of conversion increased. The activation energy finally decreased, and the curve displayed a convex shape at the high degrees of conversion, implying that the reaction changed from a chemically-controlled regime to a diffusion-controlled regime [16,17]. This trend was not observed for the oven-dried mixture, probably because the reaction for the oven-dried mixture was conducted within the diffusion-controlled regime in the whole process, or because the increase of the activation energy induced by the decomposition of biuret masked this trend in that case.

The variation in peak conversion ( $\alpha_p$ ) with the heating rate can also reflect the transition of the reaction features as illustrated in Fig. 6. The peak conversion increased with the increase in the heating rate for the oven-dried mixture, while first increased with the increase in the heating rate from 2 to 5 °C/min and then decreased slightly with the increase in the heating rate from 5 to 10 °C/min when the mixture contained 6% moisture. Furthermore, the peak conversion decreased with the increase in the heating rate when the moisture content reached 12% and above.

The curing process of the pMDI/wood mixtures under an isothermal temperature of 120 °C condition was predicted from the non-isothermal data as shown in Fig. 7. The curing rate increased when the moisture content increased. The curing process became very fast

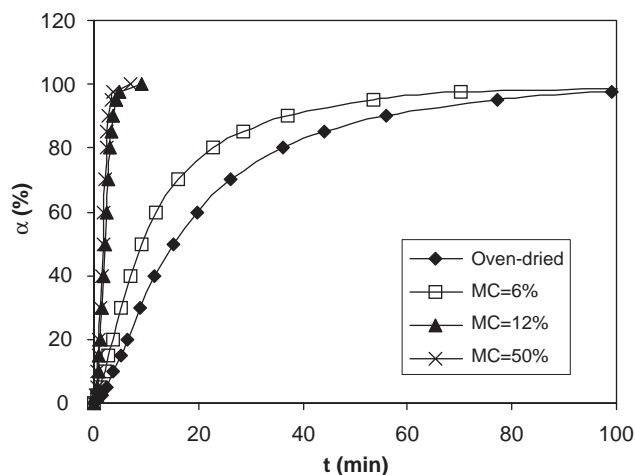


Fig. 7. Prediction of isothermal curing process at the temperature of 120 °C.

when the moisture content reached 12% and increased only slightly after the moisture content reached 12%. This result was consistent with the rate constant data obtained from the peak temperature. It implied that the amount of water in the wood was sufficient for reacting with the isocyanate when the moisture content reached around 12% for the 50/50 resin/wood mass ratio used in this study.

#### 4. Conclusions

Generally, isocyanate may react with both the hydroxyls and water in the pMDI/wood mixtures. The reaction of isocyanate with water is preferred to the reaction with the hydroxyls due to the low mobility of the hydroxyls in wood. This led to the significant influence of the moisture content in wood on the curing kinetics, in terms of DSC curve, activation energy, reaction enthalpy, and reaction rate.

For the oven-dried wood/pMDI mixture, the reaction of isocyanate occurred mainly with the hydroxyls and limited bonded water. The activation energy, reaction enthalpy, and reaction rate all had lower values because the curing process was controlled by diffusion in the absence of moisture. After moisture was introduced into the wood, the reaction of isocyanate with water was dominant. Model-free kinetics indicated that different reactions occurred in the curing process of the resin/wood mixtures when they contained moisture and when

they did not. The activation energy was lower for the oven-dried mixture than for the mixture with a moisture content of 6%. When the moisture content was above 6%, the activation energy decreased with the further increase in moisture content. Both the reaction enthalpy and the reaction rate increased with increase in moisture content. It should be noted that both the reaction enthalpy and the reaction rate remained unchanged or only increased slightly after the moisture content reached 12%.

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