Kinetic Model for the Decomposition Rate of the Binder in a Foundry Sand Application

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Abstract

Accurate kinetic parameters are vital for quantifying the effect of binder decomposition on the complex phenomena occurring during the casting process. Commercial casting simulation tools often use simplified kinetic parameters that do not comprise the complex multiple reactions and their effect on gas generation in the sand core. The present work uses experimental thermal analysis techniques such as Thermogravimetry (TG) and Differential thermal analysis (DTA) to determine the kinetic parameters via approximating the entire reaction during the decomposition by multiple first-order apparent reactions. The TG and DTA results reveal a multi-stage and exothermic decomposition process in the binder degradation. The pressure build-up in cores/molds when using the obtained multi-reaction kinetic model is compared with the earlier approach of using an average model. The results indicate that pressure in the mold/core with the multi-reaction approach is estimated to be significantly higher. These results underscore the importance of precise kinetic parameters for simulating binder decomposition in casting processes.

Keywords: Binder, Casting, Furan, Kinetics, Decomposition

1. Introduction

Binders are an integral part of the molding materials in the sand casting process since they hold the sand grains together to form a porous material. Depending on the molding process/material, binders can be organic or inorganic (chemically bonded), or the sand grains can be held together using physical compaction forces, as in the green sand case [1]. Chemically bonded molds/cores undergo a severe thermal shock during the casting process. The heat from the molten metal results in the instant vaporization of moisture accompanied by a thermal decomposition process. The gases generated during the decomposition process affect various aspects of the casting process, such as defect formation and cooling rate, and ultimately influence the properties and quality of the castings [2, 3].

The decomposing binder and the accompanying gases have been of interest for researchers and foundrymen for environmental reasons. Researchers have therefore focused on studying the decomposition of binders using thermal analysis techniques [4-8]. However, less emphasis has been placed on the accurate determination of kinetic parameters driving the decomposition process of binders. Currently, the available casting simulation tools use an overly simplified kinetic model for the binder decomposition, resulting in less accurate prediction results. The need for accurate kinetic parameters becomes essential to estimate the decomposition behavior and thereby accurately model the sand casting process. In their work, Wewerka et al. showed how the furan resin binder thermograms show different peaks for samples prepared with differing catalyst types and concentrations [9]. With evolving binder formulations from producers, considering quality and ecological reasons, the requirement for accurate kinetic parameters becomes vital, and this work is intended to do that precisely.

Various approaches have been employed to describe the decomposition behavior of the resins in general. For instance,

Nastac et al. utilized numerical modeling to evaluate thermal decomposition [10]. Zych et al. developed a laboratory-scale experimental setup dedicated to measuring the gas generation rate [11]. Also, they quantified the generated gas amount over time through casting trials [12].

Thermogravimetric (TG) analysis with different heating rates, known as the differential or integral method, is commonly used for kinetic analysis of chemical reactions. Kinetic parameters, such as pre-exponential factor and activation energy, are often determined by running TG with different heating rates and applying integral or differential methods [8, 13-15]. However, in the case of binder decomposition for the sand mold, reactions are complex, generating different types of gases (CH_4, CO_2, CO, H_2) at varying timings and temperatures. The fundamental methodology for kinetic analysis is well-established, but resin decomposition involves a series of reactions that make it challenging to identify products and reactants accurately. The complications in reactions hinder kinetic analysis. Activation energies and pre-exponential factors are often described using polynomial equations or a single average value for dominant responses. However, such oversimplified parameter values may only capture part of the decomposition process, and it is crucial to describe it based on physics and chemistry rather than relying on empirical equations or average values.

To determine the kinetic parameters using TG analysis, researchers have used the experimental mass loss data [16]. The loss of mass as a function of time equals the product of the reaction rate, k, and the retained mass. The mass loss over time depends on the order of reaction, n. Assuming a specific number for the order of reaction has been the classical approach [17] for determining kinetic parameters.

However, n is not well defined, as observed by several authors. Kada et al., in their work [18], showed that the decomposition process for polymers is complex and may encompass several separate processes/reactions that are often difficult to distinguish. The order of reaction for these complex processes can be determined using different methods. It can be determined using the theoretical shape of the TG curve or the peaks obtained from the DTA measurements and computing the slope of the peak.

The present work aims to develop a method for evaluation of binder decomposition kinetic parameters as well as to motivate the usage of it in casting process simulation as a feasible and more accurate alternative compared to the traditional single-reaction approaches. Furthermore, the developed method should allow less implementation efforts compared to the methods based on the comprehensive chemical analysis and higher-order reactions.

A method to obtain appropriate kinetic parameters for binder materials was proposed on the example of Furan binder material. The decomposition process was categorized into multiple stages based on the TG and DTA results, as well as literature data on the decomposition behavior of Furan. Next, the kinetic parameters for each stage were derived, treating the apparent reaction at each stage as a first-order reaction. The entire process was then conceptualized as a sequence of apparent reactions, assuming that sufficient reaction products from the preceding stage are available to serve as reactants for the subsequent stage. As a motivation for the proposed apparent reaction method, the pressure change in the mold was simulated using the kinetic parameters obtained through various methodologies, including the method proposed in the present study, and the results were compared.

2. Experimental Methods

2.1. TG and DTA

Furfuryl alcohol-based resin was polymerized using an acid catalyst consisting of Benzene sulphonic acid (35–50 wt.%), Xylene sulphonic acid (25–35 wt.%), Methanol (3–10 wt.%), and Toluene sulphonic acid (<10 wt.%). Small pieces of the polymerized Furan were evaluated to study the kinetic parameters (Approximately 100 mg of the Furan sample was placed in the crucible). TG analysis and DTA were performed for the furan sample to investigate the decomposition rate of the furan during the heating process. The analysis was conducted using the TG-DTA apparatus (Derivatograph C/PC, MOM Szeviz Kft.). The temperature was increased from 298 K to 1173 K with three different heating rates: 2 K/min, 7 K/min, and 17 K/min in the air atmosphere. The weight changes of the sample and the DTA signal were recorded on the computer against time and temperature.

3. Results and Discussion

3.1. TGA and DTA results

The results of the TG and DTA presented in Figure 1. reveal a multi-stage decomposition process with no significant intermediate stable phases for the studied Furan sample. For the kinetic analysis using the integral method, the TG and DTA measurements were carried out using different heating rates. The results of TG and DTA measurements for the heating rate, 2, 7, and 17 K/min are shown in Figures 1–3, respectively.
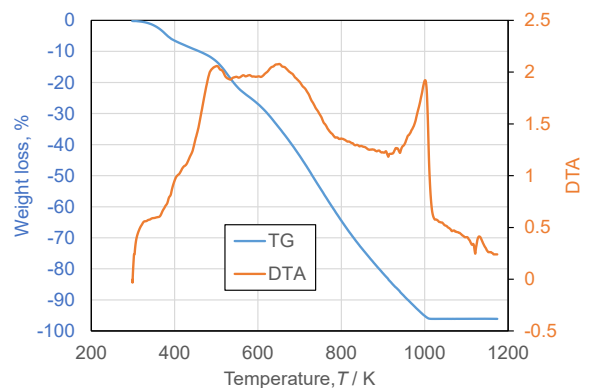

Fig. 1. TG and DTA results at heating rate 2 K/min

At roughly 373 K, the polymerized Furan binder is seen to be losing mass due to the vaporization of moisture in the form of crystalline water and free moisture. The degradation reactions happen above roughly 450 K and continue roughly until 1000 K. The DTA results show that the decomposition of the Furan binder is predominantly exothermic. Depending on the heating rates, at least three distinct enthalpic peaks could be identified from the DTA results for the different heating rates.
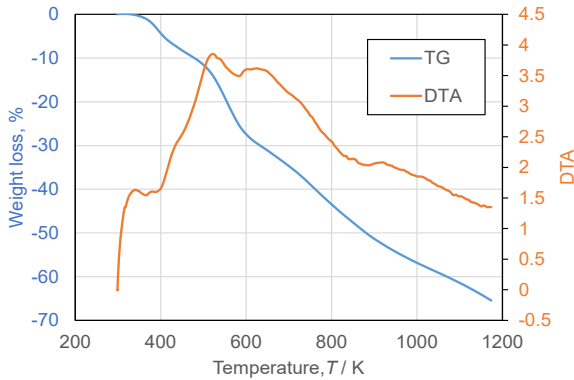

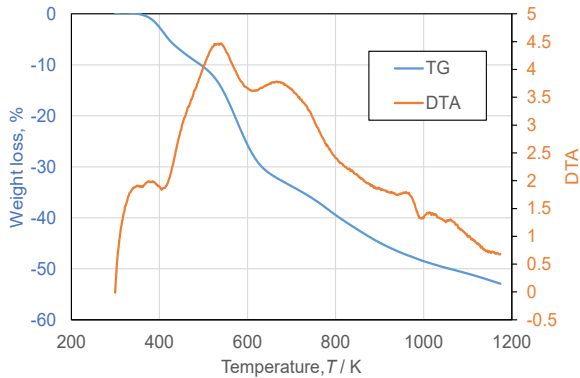Fig. 2. TG and DTA results at heating rate 7 K/min

Fig. 3. TG and DTA results at a heating rate of 17 K/min

3.2. Kinetic analysis

In the present study, the five apparent reactions at five different weight loss ranges were identified based on the TG and DTA analyses for the kinetic analysis of the gas generation rate. The apparent reactions are shown in Table 1.

Table 1.
Five apparent reactions classified by weight loss and associated gas generation

Apparent reaction	Weight loss (TG range)	Associated gas generation
1	From 0 to –8%	CH_4
2	From –8 to –20%	CH_4, CO_2, CO
3	From –20 to –35%	CH_4, CO
4	From –35 to –60%	H_2, CO
5	From –60 to –100%	H_2

Takamura [19] investigated the type of gases generated at different temperature ranges for furan, and the results are summarized in . Similar results were obtained by Fitzer et al. [20, 21] and Shinada et al. [22]. Referring to the data shown in Table 2, the associated gas generation for each reaction are summarized in Table 1 to motivate the classification of the apparent reactions.

Table 2.
Generated gases by the decomposition of furan and the temperature range [19]

Gas	Temperature range, K
CH_4	473–773
CO_2	523–673
CO	573–973
H_2	723–1223

The decomposition rate of the binder is expressed as Equation 1.

$$\frac{dx_g}{dt} = k(1 - x_g)^n \tag{1}$$

where $k = A \exp\left(-\frac{Q}{RT}\right)$, x_g is the fraction of gas (decomposed binder), t is the time, n is the order of reaction, Q is the activation energy, A is the pre-exponential factor, R is the gas constant, T is the temperature, k is the reaction rate constant,.

Hence,

$$\frac{dx_g}{(1 - x_g)^n} = \frac{1}{\frac{dT}{dt}} A \exp\left(-\frac{Q}{RT}\right) dT \tag{2}$$

where $\frac{dT}{dt}$ is the heating rate.

By assuming that the activation energy, Q, does not depend on x_g, Equation 3 will be obtained by integrating from $x_{g,0}$ to x_g and from T_0 to T.

$$\int_{x_{g,0}}^{x_g} \frac{dx_g}{(1 - x_g)^n} = \frac{1}{\frac{dT}{dt}} \int_{T_0}^{T} A \exp\left(-\frac{Q}{RT}\right) dT$$
$$= \frac{1}{\frac{dT}{dt}} \cdot \frac{AQ}{R} \cdot P\left(\frac{Q}{RT}\right) \tag{3}$$

where $x_{g,0}$ is the initial fraction of decomposed binder (i.e., 0) and T_0 is the starting temperature of the reaction. The P in Equation 3 is expressed as follows.

$$P(u) = \exp(-u)u^{-1} - \int_u^{\infty} \exp(-u) u^{-1} du \tag{4}$$

By taking the logarithm of Equation 3, we obtain

$$\log \int_{x_{g,0}}^{x_g} \frac{dx_g}{(1-x_g)^n} = -\log \frac{dT}{dt} + \log\left(\frac{AQ}{R}\right) + \log P\left(\frac{Q}{RT}\right) \quad (5)$$

The following Doyle's approximation is available when $28 \leq \frac{Q}{RT} \leq 50$,

$$\log P\left(\frac{Q}{RT}\right) \approx -2.315 - 0.4567 \frac{Q}{RT} \quad (6)$$

Hence, Equation 5 may be approximated as

$$\log \int_{x_{g,0}}^{x_g} \frac{dx_g}{(1-x_g)^n} = -\log \frac{dT}{dt} + \log\left(\frac{AQ}{R}\right) - 2.315 \\ - 0.4567 \frac{Q}{RT} \quad (7)$$

Hence, the relationship between the heating rate $\left(\frac{dT}{dt}\right)$, activation energy, Q, and the fraction of reaction product, x_g can be expressed as

$$\log \frac{dT}{dt} = \left(-\log \int_{x_{g,0}}^{x_g} \frac{dx_g}{(1-x_g)^n} + \log\left(\frac{AQ}{R}\right) - 2.315 \right) \\ - 0.4567 \frac{Q}{RT} \quad (8)$$

Therefore, by plotting the logarithm of the derivative of temperature with respect to time $\left(\log \frac{dT}{dt}\right)$ against the reciprocal of temperature $(1/T)$, the value of $-0.4567 \frac{Q}{R}$, and consequently the activation energy, Q, can be determined from the slope. The only unknown variable in Equation 8 is now the pre-exponential factor, A. The value in the bracket on the right-side of Equation 8

corresponds to the intercept of the plot, allowing the determination of the A value at the respective x_g.

As an example, the $\log \frac{dT}{dt}$ against $1/T$ was plotted using the TG data for the apparent reaction 2 (occurring between -8% and -20% weight loss)(Figure 4). It was done by assuming a first-order reaction, aiming to determine the effective A and Q values. The units of the temperature and heating rate are K and K/s, respectively.
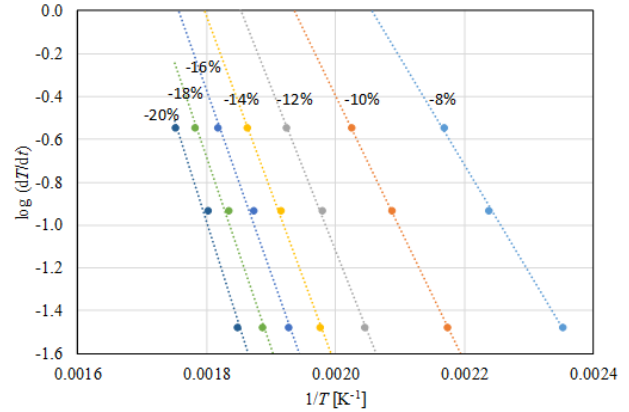

Fig. 4. Linear regression analysis for the determination of the activation energy Q, and pre-exponent factor A (Reaction 2)

In an ideal case, the activation energy Q and pre-exponent factor A should be constant, and thus the average values are taken for the specific reaction. In the case of Reaction 2 (-8 to -20% weight loss), the obtained, $Q = 1.406 \times 10^5$ and $A = 1.234 \times 10^{13}$. In the same way, the data for the other reactions (other TG ranges) were also analyzed. The analysis results are summarized in Table 3.

Table 3.
Activation energy Q and the pre-exponent factor A for each reaction (each TG range) and corresponding temperatures

Apparent reaction	Weight loss (TG range)	Corresponding temperature [K]	A [s^{-1}]	Q [J·mol^{-1}]
1	From 0 to -8%	R.T. $-$ 424	1.101×10^7	7.424×10^4
2	From -8 to -20%	424 $-$ 542	1.234×10^{13}	1.406×10^5
3	From -20 to -35%	542 $-$ 653	4.750×10^{20}	1.882×10^5
4	From -35 to -60%	653 $-$ 778	26.29	5.568×10^4
5	From -60 to -100%	778 $-$ Max.	7.726×10^{-2}	4293

The resulting pre-exponential factor, A, and the activation energy, Q, for the apparent reactions were then used to compute gas pressure inside a sand core/mold during the casting process.

As described above, in the present analysis, the integral method was adopted. For the kinetic analysis, the differential method (also known as Friedman analysis) is also often used. However, the differential method requires precise measurements (our samples are industrial and dirty, so accurate measurements cannot be expected). The Friedman method also involves complex calculations, so for simplicity, the integral method was adopted. Although the integral method has constraints/assumptions (such as

reaction mechanisms) compared to the differential method. In the present study, we are treating the reactions as apparent reactions, and thus the integral method poses no problem. Furthermore, the method to describe the decomposition kinetics of the binder proposed in this study is not intended to clarify the reaction mechanism but to propose a method to describe the reaction rate in a practical way so that one can use the method, for example, in casting simulations.

3.3. Motivation of the multi-reaction approach to binder decomposition

With the aim to motivate the multi-reaction binder decomposition as the contributor to the pressure variation in the sand core, a simplified finite-element model has been developed in COMSOL Multiphysics. It accounts for the heat transfer and the Darcian gas flow in the porous sand core. The kinetic parameters obtained by the above-mentioned TG experiments were employed to define a distributed gas source due to the decomposition of the binder at different locations and at different times. In the simulation, the gas source for each apparent reaction is activated at the its corresponding temperature, Table 3.. In the calculation, the simplified core geometry was considered (Figure 5). The boundary conditions were specified for the metal-core interface (melt temperature, T_{melt}, and no-flow condition) and for the core-air interface (room-temperature of the air, T_{air}, and atmospheric pressure, p_{atm}). The symmetry boundary conditions were applied on the other core faces.

The total pressure at the monitor point (MP) located at 1 mm from the metal-core interface was calculated, with the assumption that the temperature of the core is suddenly raised to T_{melt}, as the melt is in contact with sand during the mold filling.
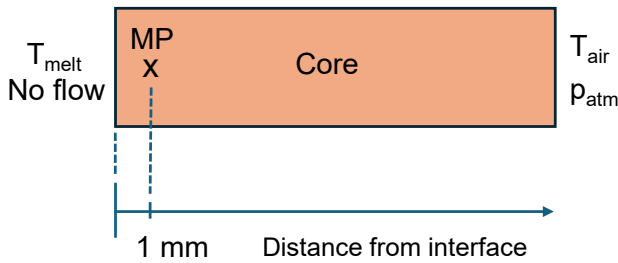

Fig. 5. Simplified core model with boundary conditions

The kinetic parameters and Equation 1 mentioned above provide the data on the gas generation (mass source). Consequently, it needs to be converted to volume to estimate the pressure change in the mold/core resulting from the decomposition.

According to Shinada et al. [22], the gas composition of the decomposed furan binder under nonoxidizing conditions is approximately 40 mol% H_2, 25 mol% CO, 17 mol% CO_2, 8 mol% CH_4, 6 mol% N_2, and 4 mol% other gases. Standardizing the composition of H_2, CO, CO_2, CH_4 and N_2 for 100 mol% and converting it to mass%, it becomes 4.4 mass% H_2, 38.4 mass% CO, 41.0 mass% CO_2, 7.0 mass% CH_4 and 9.2 mass% N_2. Thus, the molar mass of the gas mixture is 19.0 g/mol. Assuming it is an ideal gas, the density at 0 °C and 10^5 Pa, the gas density at temperature T and pressure P can be described as follows:

$$\rho(T) = \frac{M \times 10^5}{8.314T} \qquad (9)$$

where, M, is the molar mass of the gas mixture, P is the pressure in Pa and T is the temperature in °C.

The mass of the decomposed binder as a function of time was numerically calculated using Equation 1 with the A and Q values in Table 3. The density shown in Equation 9 was then employed to convert the mass to volume at temperature T and pressure P.

The variation in the calculated pressure in the mould/core against time is shown in Figure 6. In commercially available simulation software, it is common to use single A and Q values (average values). However, relying solely on such values can sometimes yield unreasonable results. To highlight the importance of considering multiple reactions (5 reactions in the present case), the pressure variation in the mold/core over time was calculated using the A and Q values of a dominant reaction (Reaction 5) in terms of the amount of the generated gas Additionally, simulation results with average A and Q values for entire process, $A = 0.02939$ and $Q = 24007$, which are obtained by the Freeman-Carroll method [23] are also shown for comparison.
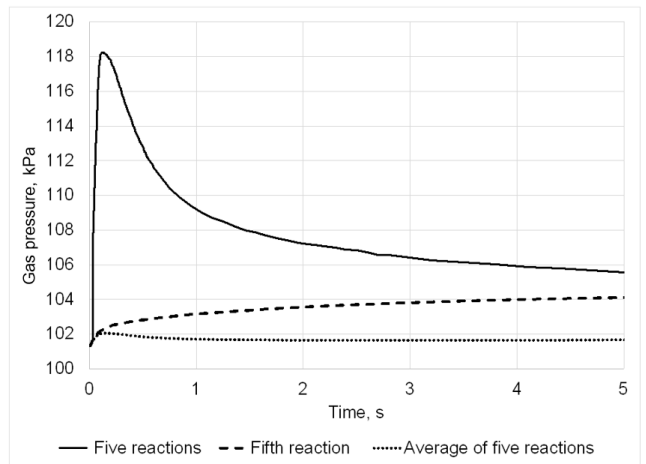

Fig. 6. Simulated pressure variation in the core at 1 mm depth, over time

As can be seen in Figure 6, the multi-reaction binder decomposition leads to a significant difference in the pressure prediction compared to the other two cases, which highlights the importance of considering the kinetics of multiple chemical reactions involved in the binder decomposition and gas generation process. The maximum difference in pressure between the average value and the value obtained by the approach suggested in the present work, which considers the multi-reaction approach, is roughly 16 kPa Underestimating the pressure build-up can cause failure to predict casting defects. Also, accurate pressure simulation can help modify or optimize the production parameters of the molds/cores. For example, in cases where the estimated pressure in the core/mold is high, production parameters such as grain size distribution, compaction force, or binder quantity can be modified to reduce the pressure build-up, thereby reducing the propensity to gas defects.

4. Conclusion

In this work, polymerized Furan resin was studied to estimate the kinetic parameters of decomposition during the sand-casting

process. The thermogravimetric and differential thermal analysis was performed for the polymerized Furan samples with different heating rates (2 K/min, 7 K/min, and 17 K/min). Since several overlapping/consecutive reactions occur during the polymer degradation, several first-order apparent reactions were assumed to drive the decomposition process, as a novel approach to the determination of kinetic parameters. This approach enabled the determination of activation energy and pre-exponential factor for the multiple apparent reactions. The proposed model does not depend on the type of binder. Furan was chosen as the exemplar binder material in this study. The obtained parameters were used to motivate the usage of multiple-reactions to compute the pressure build-up inside the cores. The results show that the pressure build-up in the multi-reaction model is significantly higher compared to the traditional simplified single-reaction approaches. It highlights the need for accurate kinetic parameters to predict the gas evolution phenomena during the sand-casting process.

The main advantage of the proposed apparent reaction approach to binder decomposition kinetics is that it allows to approximate the binder decomposition kinetics by several first-order reactions and obtain the important simulation model inputs (mainly A and Q) without the need for comprehensive chemical analysis to identify exact higher-order reactions and reaction products (gas types). At the same time, it allows to avoid oversimplification of the binder decomposition kinetics typical for single-reaction approaches.

Acknowledgement

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