

A Complete Approach for the Determination of the Heat Exchange Coefficient of a Calorimetric Reactor

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A complete approach for the determination of the heat exchange coefficient of a calorimetric reactor is presented. The results are compared to the ones that can be obtained according the usual simplified method that can be found in the literature. The accuracy is noticeably improved and it justifies the higher effort if this method.

1. Introduction and theoretical approach

The study of heat exchange is fundamental to perform an accurate thermal study in a calorimetric, jacketed, stirred tank reactor. Moreover, since cooling or heating in a jacketed stirred reactor is an indispensable operation to control a process, the knowledge of the rate of the heat exchange is needed. In this way, the heat exchange coefficient should be determined with a good precision.

In the literature, a theoretical semi-empirical approach is provided by Sinnot (2005), who provides a set of correlations by mean the heat exchange coefficient can be calculated. Each correlation is valid for only a kind of impeller. Several articles deal with the empirical determination of the heat exchange coefficient, as the case of Raguraman *et al.* (2012), Dostàl *et al.* (2010) or Debab *et al.* (2010).

Essentially, all the methods are obviously based on the enthalpy balance as Eq(1):

$$m \cdot cp \cdot \frac{dT}{dt} = -U \cdot A \cdot (T - T_{jacket}) + \dot{Q}_s + \dot{Q}_r \quad (1)$$

in which $m \cdot cp$ [J/K] is the heat capacity of the mixture and the impeller, both contained in the reactor. $U \cdot A$ [W/K] is the product of the heat exchange coefficient and the area, \dot{Q}_s, \dot{Q}_r [W] are the heat exchanged with surroundings and the heat developed by the reactions, respectively. The way in which this balance is exploited makes the difference between each method. For example, according Debab *et al.* (2010), the time evolution of the temperature during a heating can be linearized in such a way the time derivative of the temperature can be estimated in a simple way. Moreover, the heat capacity of the impeller is neglected, considering the one of the mixture only. In this way $U \cdot A$ is determined. However, both these approximations lead to a loss on accuracy. Another classical simplified route consists in the generation of some thermal power in the reactor using an electric heater, until the steady state is reached, as the case of De Quadros *et al.* (2015), Casson (2012) and Ampelli (2006). The temperature in the reactor is measured and, performing a fitting on the cooling transient, the time constant of the thermal process is estimated. The time evolution of the temperature is assumed exponential because, integrating Eq. (1), equation (2) can be obtained:

$$\frac{T(t) - T_{jacket}}{T(t_0) - T_{jacket}} = e^{-\frac{U \cdot A}{m \cdot cp}(t - t_0)} = e^{-\frac{t - t_0}{\tau}} \quad (2)$$

where the time constant τ [s] is equal to $\frac{m \cdot cp}{U \cdot A}$.

Once the time constant is determined by fitting, to obtain $U \cdot A$, the heat capacity of the mixture inside the reactor must be known. In this work, it is demonstrated that this approach cannot work with a good accuracy, since the effective heat capacity must consider also the contribute of the metallic impeller or other instrumentations.

The approach used in this work considers both the thermal steady state and the cooling transient since different information can be drawn from both. From the steady state, $U \cdot A$ can be determined as Eq. (3).

$$Q = U \cdot A \cdot (T - T_{jacket}) \quad (3)$$

Once the time constant is determined from the cooling transient, the effective heat capacity can be obtained substituting $U \cdot A$. However, it is reminded that if only the transient is considered, no information about the heat power generated is needed. At the contrary, with this approach the generated power must be constant and known with optimal accuracy. Consequently, a proper system is developed.

It is reminded that this work was carried out to perform a calorimetric study of the epoxidation of soybean oil using hydrogen peroxide, acetic acid and sulfuric acid as catalyst. This process is well known and described by several articles as the case of Dinda *et al.* (2007), De Quadros and Giudici (2015) and Piccolo (2016). A preliminary safety study on the decomposition of hydrogen peroxide in presence of acids was performed by Vianello *et al.* (2015).

2. Materials

About the mixture used for the tests, surely water could be used as a standard. However, this work is an auxiliary study for a correlated research on the epoxidation of soybean oil. For this reason, the employed mixture is made of acetic acid, hydrogen peroxide and soybean oil. No acid catalyst is introduced, so it can be demonstrated that no reaction takes place and no heat is generated by reactions.

The acetic acid 98% and the hydrogen peroxide 34% are purchased from *Sigma-Aldrich*. Soybean oil at food grade is purchased in a local supermarket.

3. Instrumentation

The employed reactor is a batch, stirred and jacketed tank by *BüchiGlasUster* (Figure 1 a). It permits to record temperatures and pressure to perform calorimetric analysis. The temperature control of the reactor is ensured by the silicone oil that flows in the jacket and a thermocryostat by *Huber* (Figure 1 b). This apparatus permits to set a temperature program with excellent accuracy. Three thermocouples Pt100 are installed in the reactor and at the inlet and at the outlet of the jacket. A pressure transducer is installed in the reactor, whereas a rupture disc guarantees the safety of the equipment. An analogic manometer permits to monitor the pressure in the case the pressure transducer is not working. A stack of electronic analog to digital converters (by *National Instrument*) permits to collect data of the three temperatures and of the pressure and to send them to a PC via USB port. An *ad hoc* software realized using *LabView* (*National Instrument*) is used to record data and to visualize them on a monitor in real time.



a)



b)

Figure 1. a) Calorimetric reactor by BüchiGlasUster. b) Thermocryostat by Huber used for the determination of the heat exchange coefficient.



a)



b)

b)

Figure 2. a) Ceramic heater b) Automatic power controller, used for the determination of the heat exchange coefficient.

As regards the stirring system, a Rushton turbine is used to create a good emulsion between the organic and the inorganic phases. The shaft of the impeller is magnetically coupled to the electric motor, in such a way that sealing is guaranteed. The motor is controlled by an electronic interface that permits a precise regulation by software.

For the generation of the thermal power in the reactor, a 3D printer ceramic heater is chosen (Figure 2 a). This kind of heater has small dimensions (20 mm of length and 6 mm diameter), very low cost, low voltage (24V DC) and good power (40 W nominal). It is reminded that, during the operation of this resistor, the internal resistance and consequently the absorbed electrical power can change. In this way, a constant well determined thermal generation (that is indispensable to solve equation (3)) can result quite difficult. Moreover, the possibility of changing the generated power is considered, to evaluate its influence in the heat exchange coefficient. For both reason, a simple DC regulated power supply is not enough. In fact, in addition to it, a precise automatic power controller (Figure 2 b) was designed and built. This device is based on an ATmega328 microcontroller and accurately controls the power generated by the heater. The user can set the desired power on it.

3.1 Automatic power controller

For the reasons earlier explained, an automatic power controller (Figure 2 b) is needed. This system was design and built ad hoc.

The control is achieved using a feedback controller. In fact, the measured instant power that is applied to the resistor is compared with the desired power (setpoint) and, on the base of this difference, the microcontroller adjusts the voltage applied to the resistor. This system is made of many units:

- a data collector unit that measures both the voltage applied at the resistor and the current flowing through it. The data are digitalized by an ADC (analog to digital converter);
- a controller unit that computes the power applied to the resistor in each instant. After a comparison with the setpoint power, the microcontroller takes a decision and send a PWM (pulse width modulation) output signal to the converter unit;
- a converter unit that takes the signal from the microcontroller and converts it into an analog signal;
- an actuator that brings the voltage applied to the resistor to the value set by the microcontroller.

The system is based on a platform called Genuino (Arduino) that mounts an ATmega 328 microcontroller.

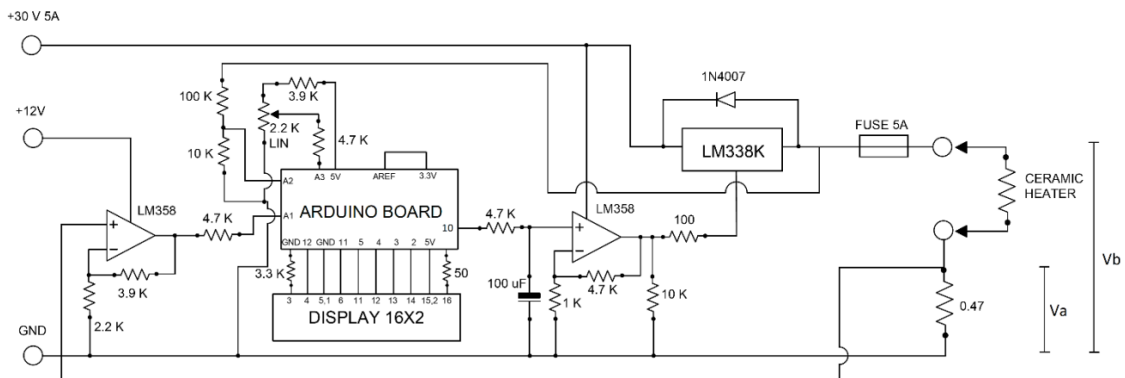


Figure 3. Schematic diagram of the automatic power controller.

As can be seen from the schematic (Figure (3)), both the current flowing through the ceramic heater and the voltage across it are indirectly measured. In order to obtain these two data, two voltages are measured, V_a and V_b . V_a is amplified by an operational amplifier LM358 with a gain of about 2.8 and sent to the microcontroller (input A1). V_b is divided by a voltage divider (1:11 ratio) to low the voltage and it is sent to the microcontroller (input A2). After a calibration and a fitting of the data performed using *Matlab* (by *Mathworks*), it is possible to obtain the two calibration curves related to the current (function of V_a) and the voltage across the ceramic heater (function of (V_b and V_a)). Thanks to an algorithm stored into the flash memory of the microcontroller, the two information on current and voltage are computed by mean of the two calibration curves. After that, the electrical power absorbed by the heater is calculated. This result is compared with the power setpoint set by the user (acting on the potentiometer) and the error is calculated as Eq. (4)

$$e = P_{setpoint} - P_{real} \quad (4)$$

On the base of the error, the algorithm acts on the duty cycle of the PWM control signal sent to pin 10. The duty cycle is stepwise changed so that the larger is the error, the faster is the control. The control signal is filtered and amplified and then sent to a linear voltage regulator (LM338K). In conclusion, the values of power setpoint, read power, current and voltage are indicated on the 16X2 lcd display.

4. Procedure

The reactor is loaded with 205.6 g of mixture made of 7.7wt.% of acetic acid, 40.9wt.% of hydrogen peroxide and 51.4wt.% of soybean oil. The ceramic heater is fastened and the stirring is switched on at 500 rpm. The thermocryostat is set to 60°C. After that, a sufficient time is required in such a way the transient is extinguished and the steady state is reached. The desired power is set on the power controller and a new steady state is reached. After that, the ceramic heater is switched off and the initial steady state is reached ($T=60^\circ\text{C}$). The experiment is repeated for different values of generated power.

5. Results

5.1 Study on the cooling transient

As regards the cooling transient, the determination of τ is carried out by passing to logarithms the equation 3. In this way, it is possible to obtain Eq. (5):

$$\ln(T(t) - T_{jacket}) = -\frac{t - t_0}{\tau} + \ln(T(t_0) - T_{jacket}) \quad (5)$$

In this way, Eq. (5) is a linear function of $\frac{1}{\tau}$. Generating some thermal power inside the reactor, as described earlier, the collected data of temperature are elaborated in order to compute the difference $T(t) - T_{jacket}$, i.e. $\Delta T(t)$, in which t is a generic instant. Successively $\ln(T(t) - T_{jacket})$ is calculated and a linear fitting is performed. This procedure is repeated for different values of thermal power, 20, 25 and 35W. Only one test and its fitting is reported in Figure 3. All the results are summarized in Table 1.

Table 1: Values of τ and $\frac{U \cdot A}{m \cdot cp}$ obtained by fitting of data using power 20, 25, 35 W.

Power [W]	τ^{-1} [min^{-1}]	τ [min]	$\tau^{-1}[\text{s}^{-1}] = \frac{U \cdot A}{m \cdot cp}$	τ [s] = $\frac{m \cdot cp}{U \cdot A}$	R^2 [-]
20	0.5942	1.683	0.009903	101.0	0.99997
25	0.6084	1.644	0.01014	98.62	0.99992
35	0.6004	1.666	0.01001	99.94	0.99984
Mean value	0.6010	1.664	0.01002	99.85	-

As concerns the fitting, in the case of 20, 25 and 35W the values of τ are 0.5942, 0.6084 and 0.6004 min^{-1} . These values are very similar, even though they are obtained with different power. This fact confirms the quality of these data. Moreover, the fitting is very good, since R^2 is greater than 0.999. In the first two cases, R^2 is even greater than 0.9999.

In conclusion, the mean value 99.85 seconds is considered. This values indicates that the transient extinguishes after 400-500 seconds ($4-5\tau$). The table indicates τ and τ^{-1} with the units of measurement of minutes or seconds. The value is transformed from minutes to second in order to report it in International System of Units. In this way, calculation of $U \cdot A$ and $m \cdot cp$ are direct and simpler.

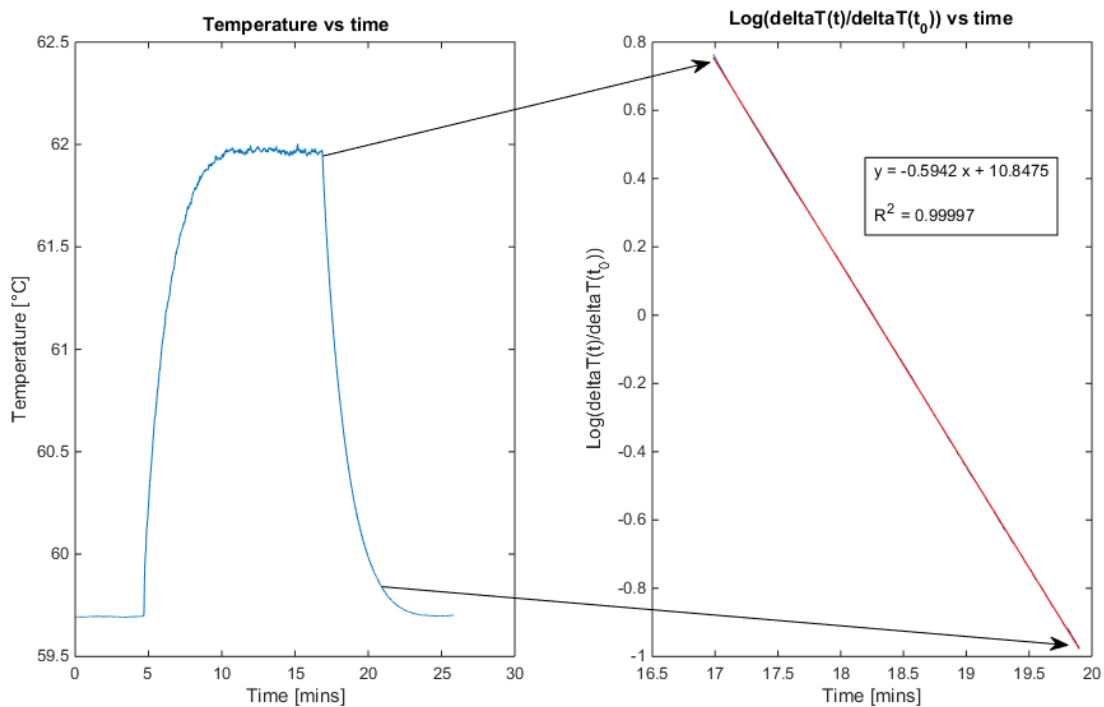


Figure 3. Left: thermal transient obtained generating a thermal power of 20W inside the reactor. Right: logarithm of $\Delta T(t)$ (blue) and its fitting (red). τ^{-1} equal to 0.5942 min^{-1} . R^2 equal to 0.99997.

5.2 Study on thermal steady state

As concerns the thermal steady state, data obtained with 20 and 25 W are considered. In these case, the values of temperature at the steady state are 61.97 and 62.5478 °C. Using equation 4 it is possible to obtain $U \cdot A$. Table 2 indicates the results.

Table 2. Values of temperature in the reactor and in the jacket and $U \cdot A$. Tests at 20 and 25 W.

Power [W]	T [°C]	T _{jacket} [°C]	ΔT [°C]	$U \cdot A$ [W/K]
20	61.97	59.65	2.32	8.62
25	62.55	59.65	2.90	8.62
Mean value				8.62

From the previous table, it can be noticed that the value of $U \cdot A$ determined for the two value of power are very similar. This fact confirm that data is good. The mean value of 8.62W/K is considered. For the sake of correctness, it is to remind that $U \cdot A$ could be determined from the value of $\frac{U \cdot A}{m \cdot cp}$ previously determined by simple substitution of the value of $m \cdot cp$ of the mixture. This approach is not completely correct because the impeller inside the reactor has its own heat capacity. Moreover, this approach does not consider the value of the heat losses of that part of the reactor that are not covered by the jacket. At the contrary, with the approach employed in this work, $U \cdot A$ is computed in the steady state and on the base of this value and the one of τ determined in the cooling transient, the effective $m \cdot cp$ can be computed. This value is not the theoretical one but the effective one, since it includes the capacity of the impeller and the losses.

On the base of τ and $U \cdot A$, the value of $m \cdot cp$ results equal to 861 J/K. Knowing that the heat specific capacity is 3.014 J/gK (USP Technologies, 2016), 1.875 J/gK (NIST, 2016) and 2.32 J/gK (Hammond et al, 2005) for hydrogen peroxide 32%, soybean oil and acetic acid respectively the theoretical heat capacity is 488 J/K (ideal mixture). This value is much lower than the one determined with our method (861 J/K) for the reason previously exposed. Consequently, if the only cooling transient were considered, with the determined τ and the estimated capacity, the product $U \cdot A$ would be 4.892 [W/K]. This means that the error would be equal to 43.3%. This result demonstrates that this approach, that uses both steady and transient data, is much more accurate than the one based solely on the transient. Moreover, the ϕ -factor of the reactor can be calculated according Eq. (6):

$$\phi_{factor} = \frac{\text{heat capacity of mixture and reactor}}{\text{heat capacity of mixture}} \quad (6)$$

The factor is equal to 1.76, noticeably greater than 1. This confirms that heat capacity of the reactor is not negligible.

In conclusion, Table 3 summarizes the results obtained in this paragraph.

Table 3. Values of τ , τ^{-1} , effective and theoretical heat capacity.

τ [s] = $\frac{m \cdot cp}{U \cdot A}$	τ^{-1} [s ⁻¹] = $\frac{U \cdot A}{m \cdot cp}$	$U \cdot A$ [W/K]	Effective heat capacity [J/K]	Theoretical Heat capacity [J/K]
99.85	0.01002	8.630	861	488

6. Conclusions

Thanks to this complete approach, both the heat exchange coefficient and the heat capacity are well determined. Moreover, the values of τ , $m \cdot cp$ and $U \cdot A$ remain constant even if the generated thermal power is varied. This fact is very important and it represents a proof to the affordability of these results. In addition, comparing these results to the ones obtained with the simplified method, the error is noticeably reduced (43.3%). In fact, since the ϕ -factor (1.76) is high, the heat capacity of the reactor is not negligible. In consequence, both the steady state and the transient must be considered to carry out calculation, otherwise a large error would be committed. In this way, good data useful for future thermal characterization of reactions carried out in this reactor are available. Moreover, the higher effort for the design and the realisation of the automatic power controller are well payed off. As a future perspective, a different implementation of the automatic controller could be considered to increase the accuracy and to improve the control.

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