CHAPTER 2

Experimentation

2.1 Materials

2.1.1 **Raw material**

2.1.1.1 Commercial CPO (~5 wt% of FFA) purchased from a local palm oil mill was used as feedstock for the experimentation.

2.1.2 **Chemicals**

2.1.2.1 Ethanol (C_2H_5OH) 99.5 wt% commercial grade

2.1.2.2 Sulfuric acid (H_2SO_4) 98 wt% commercial grade

2.2 Equipment and instrument

2.2.1 Ultrasonic processor, model UP400S, 24 kHz, 400 W. produced by Hielscher, Germany fitted with a 22 mm diameter sonotrode was used as the ultrasound generator. It can be adjusted to produce varying amplitude across a full range up to a maximum of 100 micrometers and has an acoustic power density of 85 W/cm^2 and a maximum submerged depth of 45 mm. This ultrasonic processor was used for batch ultrasonic experiments.

2.2.2 Ultrasonic processor: model YPSH1020204, 20 kHz, 1000 W (including transducer with cover, booster, titanium horn and generator) produced by Hangzhou Success Ultrasonic Equipment Co., Ltd., China. This ultrasonic processor was used for continuous ultrasonic experiments.

2.2.3 A 400-mL glass reactor, (ID: 60 mm, height: 155 mm) with a plastic sealed lid was used as the esterification reactor for the batch ultrasonic experiments. The attachment between the sonotrode and the glass reactor lid was sealed with a synthetic rubber o-ring in order to prevent any gas leakage.

2.2.4 A 4.60 L stainless steel reactor, 97 mm ID, 700 mm in length was used for continuous ultrasonic experiments.

2.2.5 A 1.47 L stainless steel reactor, 61 mm ID, 700 mm in length was used for continuous ultrasonic experiments.

2.2.6 A 87.4 L continuous stirred-tank reactor (CSTR), 310 mm ID and 1200 mm in length, a baffle tank equipped with 3-levels blade (6 blades), (details of the reactor were shown in appendix D) was used for CSTR experiments.

2.2.7 A water chiller controlled by a thermostat was provided by the Scientific Equipment Center, PSU, Songkhla, Thailand.

2.2.8 A cooling bath, a plastic container, inner diameter of 100 mm, height of 140 mm.

2.2.9 A water circulating pump was used as the temperature controlling system and assembled in the cooling bath.

2.2.10 Digital dosing pumps, model DMS and DME, Grundfos, Germany used for feeding CPO and ethanol-acid mixture.

2.2.11 A 17 L stainless steel heater tank equipped with 3 kW coiled heater used for heating CPO, as external heating source before feeding to CSTR.

2.2.12 A temperature monitoring was carried out using a Templog Temperature Data Logger version 1.0 digital thermometer with 8 channels purchased from the Scientific Equipment Center, PSU, Songkhla, Thailand. The thermometer probe was dipped into the reaction solution. The equipment was set up as shown in the experiment schematic diagram (Fig. 2.1).

2.2.13 A watt hour meter, type PL 10053, was used to monitor the power consumption.

2.2.14 An infra red thermometer, model DP-88, DIGICON

2.2.15 A hot air oven, model UNB 400, MEMMERT

2.2.16 A household microwave was used to dry the samples

2.2.17 A raw material feed tank

2.2.18 An ethanol-acid mixture feed tank

2.3 Methodology

2.3.1 **Studies of batch acid catalyzed esterification of CPO with ethanol assisted by ultrasonic irradiation**

The batch esterification equipment was set up as showing in Figure 2.1. The esterification reactions were carried out in the glass reactor placed in a circulating water bath. Chilled water was circulated from water chiller by a water pump. The sonotrode was submerged in the reaction solution to a depth of 20 mm. The reaction temperature was controlled by adjusting flow rate of the cooling water and monitored by using the digital thermometer. The temperature was periodically recorded throughout the experiments.

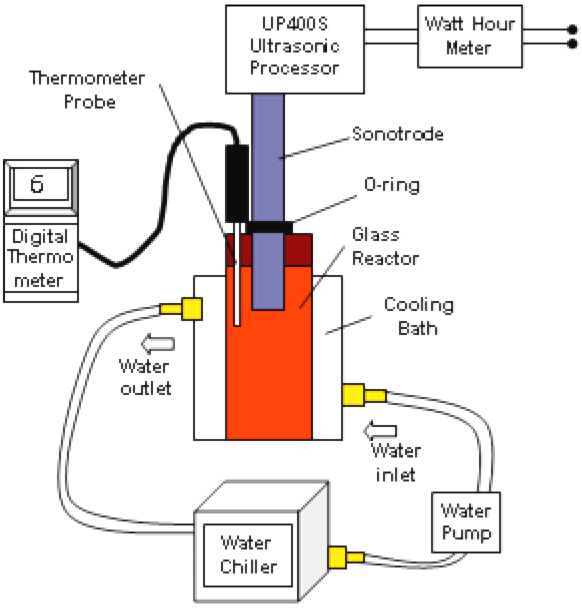

Figure 2.1 Schematic diagram of the batch esterification

Figure 2.2 Equipment setup of the batch esterification

Details of the experiments were stepwise described below.

2.3.1.1 Preliminary experiments. The experiments were designed by using Taguchi method (Peace, 1993) applying five randomly selected factors at four levels (Table 2.1). The preliminary experiments produced an $L_{16}(4^5)$ orthogonal array, corresponding to the 16 runs shown in Table 2.2.

Table 2.1 Factors and levels of the preliminary experiments

Factors	Description	Level 1	Level 2	Level 3	Level 4
Cat	: % H_2SO_4 by wt of FFA	1	2	5	20
Amp	: % Amplitude of acoustic power	35	55	75	100
MR	: Molar ratio of ethanol: FFA	5	10	20	40
Temp	: Reaction temperature in degree C	50	60	70	80
Time	: Reaction time in hour	0.5	1	2	4

Table 2.2 Orthogonal array of the preliminary experiments

Run No.	Cat	Amp	MR	Temp	Time
1	1	35	5	50	0.5
2	1	55	10	60	1
3	1	75	20	70	2
4	1	100	40	80	4
5	2	35	10	70	4
6	2	55	5	80	2
7	2	75	40	50	1
8	2	100	20	60	0.5
9	5	35	20	80	1
10	5	55	40	70	0.5
11	5	75	5	60	4
12	5	100	10	50	2
13	20	35	40	60	2
14	20	55	20	50	4
15	20	75	10	80	0.5
16	20	100	5	70	1

2.3.1.2 Secondary experiments exploiting the previous results. The secondary stage was finally defined by five re-ordered significant factors including two additional interaction factors i.e. CatxTemp and CatxMR (Table 2.3) that were needed after examining the interaction graphs obtained from the preliminary experiments. This experimental design produced a $L_8(2^7)$ orthogonal array, corresponding to the eight runs shown in Table 2.4. Both CPO and ethanol amount were fixed at 300 g per batch in order that every batch would have an equal volume optimized for the depth at which the sonotrode was submerged.

Table 2.3 Factors and levels of the secondary experiments

Factors	Descriptions	Level 1	Level 2
Cat	: % H_2SO_4 by wt of FFA	30	60
Time	: Reaction time in hour	1	2
Temp	: Reaction temperature in degree C	60	80
CatxTemp	: Catalyst interacts with temperature		
MR	: Molar ratio of ethanol: FFA	20	30
CatxMR	: Catalyst interacts with molar ratio		
Amp	: % Amplitude of acoustic power	35	75

Table 2.4 Orthogonal array of the secondary experiments

Run No.	Cat	Time	Temp	CatxTemp	MR	CatxMR	Amp
1	30	1	60	30x60	20	30x20	35
2	30	1	60	60x80	30	60x30	75
3	30	2	80	30x60	20	60x30	75
4	30	2	80	60x80	30	30x20	35
5	60	1	80	30x60	30	30x20	75
6	60	1	80	60x80	20	60x30	35
7	60	2	60	30x60	30	60x30	35
8	60	2	60	60x80	20	30x20	75

2.3.1.3 Further experiments based on the best conditions of the secondary experiments were conducted by using different reaction times.

2.3.1.4 Additional experiments were set up to investigate the effect of ester hydrolysis using two-stage esterification. The optimized conditions were based on those results from the further experiments which produced the least FFA to be used for conducting the first stage esterification. After finishing the first stage reaction, all reaction mixture was washed with warm water until obtained neutral washing water and then dried with a household microwave for 3 minutes (1.5 minute each) to insure that it had no water. Then the second esterification was conducted by using the same conditions as previously used.

2.3.1.5 The energy consumptions were recorded and compared with theoretical energy consumptions.

2.3.1.6 Phosphorus content analysis of some samples was conducted, as well as the final and initial phosphorus contents were compared. Determination of the phosphorus content was determined by the ASTM D 4951 standard method.

The batch experiment procedures were following;

1) Calculate CPO, ethanol and sulfuric acid used for each run according to their arrays. Both CPO and ethanol were fixed at 300 g per batch in order that every batch would have an equal volume optimized for the submerged depth of sonotrode.

2) Prepare ethanol-sulfuric acid solution by mixing them together.

3) Weigh CPO and put it into the reactor.

4) Pour the ethanol-sulfuric acid solution into CPO then close the reactor with its lid.

5) Put the reactor in a water bath which laid on an adjustable stand.

6) Submerge a sonotrode to the mixture until it attach closely to an o-ring over the lid.

7) Adjust the stand to ensure that there is no any gas leakage at any points.

8) Put the temperature probe to the reaction mixture through a small sealed puncture.

9) Turn on the temperature data logger and record initial temperature of the reaction mixture.

10) Connect the watt hour meter to a power line and connect an input line of the ultrasonic processor to the watt hour meter. Record initial watt hour.

11) Start irradiate ultrasound by switch on the power button of the ultrasonic processor, model UP400S and adjust amplitude (turn an amplitude knob) according the experiments.

12) Start the circulating pump to control the temperature as per the experimental design. Record the temperature periodically.

13) Stop irradiation when the reaction time is over.

14) Stop the cooling water circulation.

15) Record all parameters used and take sample to analyze FFA content.

2.3.2 Studies of continuous acid catalyzed esterification of CPO with ethanol assisted by ultrasonic irradiation.

2.3.2.1 Continuous acid catalyzed esterification at 80ºC (without controlling) with stainless steel reactor having volume of 4.6 L, inner diameter of 97 mm and length of 700 mm. The flow pattern used was vertical up flow.

2.3.2.2 Continuous acid catalyzed esterification at 80ºC (without controlling) with stainless steel reactor having volume of 1.47 L, inner diameter of 61 mm and length of 700 mm. The flow pattern used was vertical up flow.

2.3.2.3 Continuous acid catalyzed esterification at 80ºC (without controlling) with stainless steel reactor having volume of 1.47 L, inner diameter of 61 mm and length of 700 mm. The flow pattern used was vertical down.

2.3.2.4 Continuous acid catalyzed esterification at 60ºC with stainless steel reactor having volume of 1.47 L, inner diameter of 61 mm and length of 700 mm. The flow pattern used was horizontal flow. The reaction temperature is controlled at 60ºC.

2.3.2.5 The energy consumptions of each experiment were compared with the theoretical energy consumptions.

This continuous esterification experiments were concluded in Table 2.5.

Table 2.5 The continuous esterification experiments

Continuous experiments	Volume of reactors (L)	Inner diameter of reactors (mm)	Reactors' temperature (°C)	Flow patterns
1	4.6	97	80	Vertical up flow
2	1.47	61	80	Vertical up flow
3	1.47	61	80	Vertical down flow
4	1.47	61	60	Horizontal flow

For the continuous experiments, two sizes of reactors are shown in Figure 2.3 including the sonotrode used and the equipment setup is illustrated in Figure 2.4.

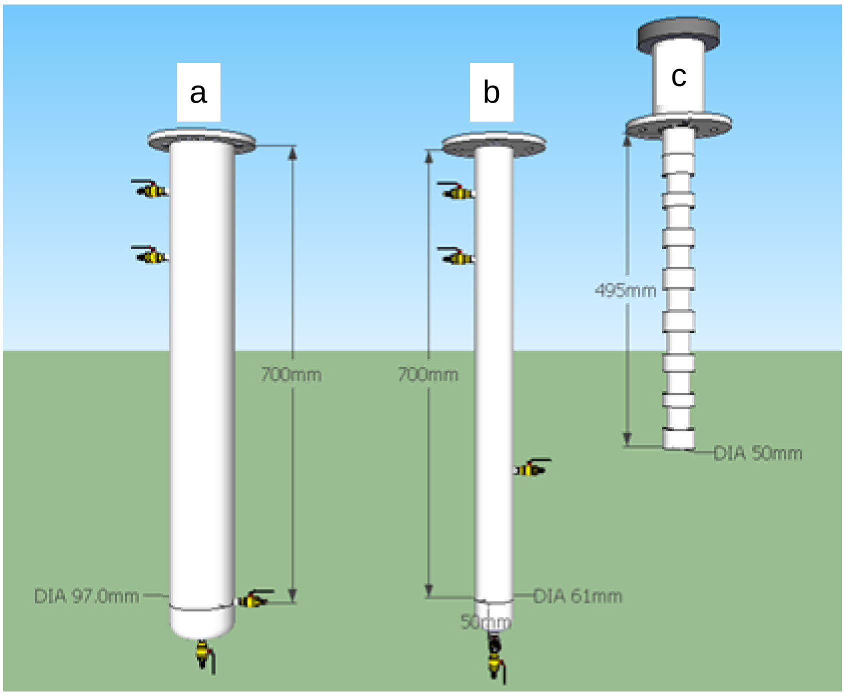

Figure 2.3 Continuous reactors (a: 4.60 L and b: 1.47 L) and a sonotrode (c)

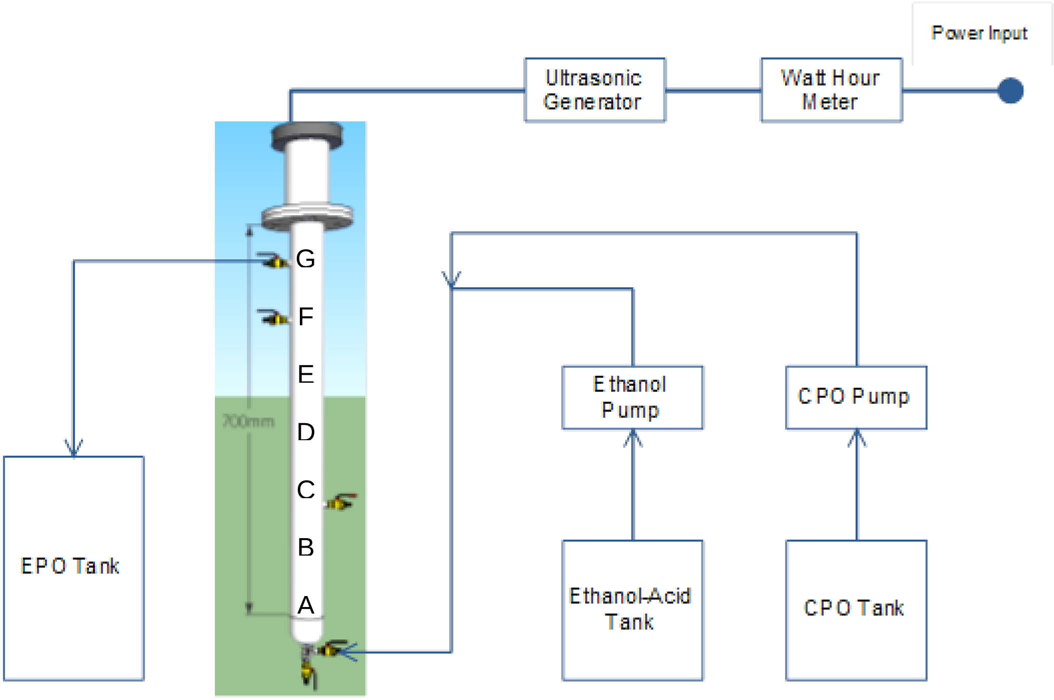

Figure 2.4 Schematic diagram of the continuous esterification (points of A, B, C, D, E, F and G are represented the temperature measuring points located 100 mm between each point)

(a) (b) (c)

Figure 2.5 A sonotrode (a), A continuous reactor (b) and an ultrasonic generator (c)

There were four experiments using different sizes of reactors and flow patterns, but all of them were performed under the same methodology as 3 factors and 2 levels shown in Table 2.6, consequently obtained the orthogonal array of $L_4(2^3)$ in Table 2.7.

Table 2.6 Factors and levels of the continuous experiments.

Factors	Descriptions	Level 1	Level 2
Cat	: % H_2SO_4 by wt of FFA	30	60
MR	: Molar ratio of ethanol: FFA	20	30
RT	: Retention time in hour	0.5	1

Table 2.7 Orthogonal array of the continuous experiments.

	Factors		
Run No.	Cat	MR	RT
1	30	20	0.5
2	30	30	1
3	60	20	1
4	60	30	0.5

The continuous experiment procedures were following;

1) Set up the equipment as per the schematic diagram in Figure 2.4.

2) Calculate CPO, ethanol and sulfuric acid used for each run according to their arrays.

3) Prepare ethanol-sulfuric acid solution by mixing them together.

4) Fill up CPO and ethanol-sulfuric acid solution into the reactor.

5) Connect the watt hour meter to a power line and connect an input line of the ultrasonic processor to the watt hour meter. Record initial watt hour.

6) Start pumping CPO and the ethanol-sulfuric acid solution to the reactor.

7) Start irradiating ultrasound by switch on the power button of the ultrasonic processor, model YPSH1020204.

8) Start the circulating (if needed) using tap water flowing through an absorbed media which fixed around the reactor to control the temperature as per the experiments. Periodically record the temperature at the reactor surface using an infra red thermometer.

9) Collect samples from an outlet valve as interval as desire.

10) Stop irradiation when the reaction time is over.

11) Stop CPO and the ethanol-sulfuric acid solution pumps.

12) Stop the circulating.
13) Record all parameters used.

2.3.3 Studies of continuous acid catalyzed esterification of CPO with ethanol using continuous stirred-tank reactor (CSTR)

This study aimed to compare with the continuous ultrasonic experiments, therefore the experimental design was performed in the same fashion of that mentioned in the continuous ultrasonic experiments. There were four experiments containing 3 factors and 2 levels shown in Table 2.8, consequently obtained the orthogonal array of $L_4(2^3)$ in Table 2.9. The reaction temperature was 60ºC, initial FFA was 6-8 wt% in range and the agitation was fixed at 700 rpm corresponding to N_{Re} of 20,249. The dimensions of this CSTR reactor are 310 mm ID and 1200 mm in length from input to output valves. It contains 87 L of volume. The schematic diagram of this experiment setup was illustrated in Figure 2.5 and details of the reactor were shown in appendix D.

Table 2.8 Factors and levels of the continuous experiments by CSTR.

Factors	Descriptions	Level 1	Level 2
Cat	: % H_2SO_4 by wt of FFA	30	60
MR	: Molar ratio of ethanol: FFA	20	30
RT	: Retention time in hour	0.5	1

Table 2.9 Orthogonal array of the continuous experiments by CSTR.

	Factors		
Run No.	Cat	MR	RT
1	30	20	0.5
2	30	30	1
3	60	20	1
4	60	30	0.5

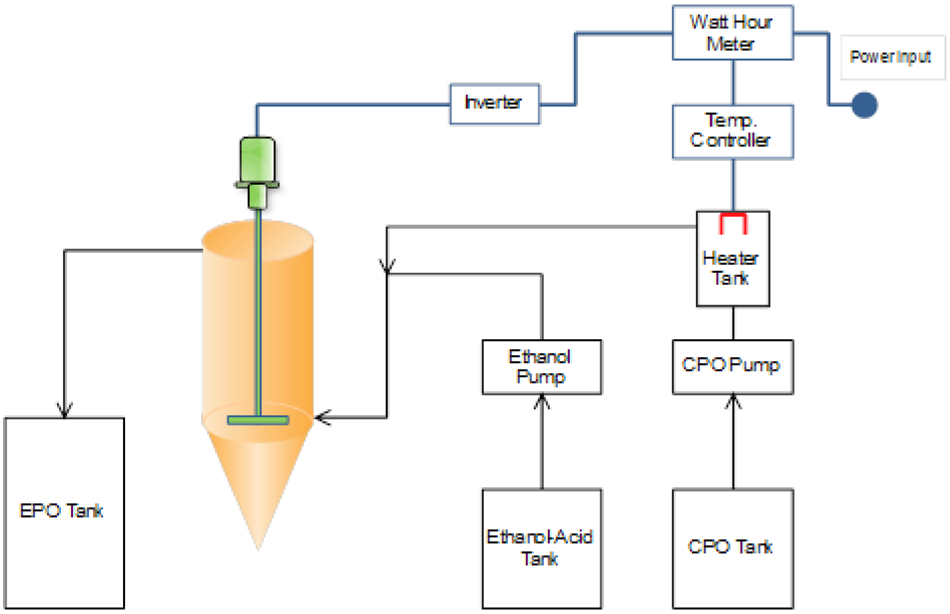

Figure 2.6 Schematic diagram of the CSTR esterification

The CSTR experiment procedures were following;

1) Set up the equipment as per the schematic diagram in Figure 2.6.

2) Calculate CPO, ethanol and sulfuric acid used for each run according to their arrays.

3) Prepare ethanol-sulfuric acid solution by mixing them together in an ethanol-acid tank.

4) Connect the watt hour meter to a power line and connect all electrical equipment from the watt hour meter. Record initial watt hour.

5) Start pumping CPO through a heater tank until it is full then stop pumping.

6) Start heating CPO till it has temperature about 75ºC.

7) Start pumping CPO and the ethanol-sulfuric acid solution to the reactor.

8) The agitation will be started after the mixture in the reactor is 1/3 in volume.

9) Record temperature at the reactor, periodically and record kWh after the experiment is finished.

10) Collect samples from an outlet valve as interval as desire.

11) Stop CPO and the ethanol-sulfuric acid solution pumps.
12) Stop the agitation.

2.4 Chemical analysis

2.4.1 For batch experiments, 30 mL samples were drawn from the final reaction mixture and immediately washed with warm water in a 250 mL separatory funnel, in order to stop the reaction and remove all contaminants such as ethanol, gum and sulfuric acid. The washing step was repeated until the washing water had a pH of 7. The clean samples containing saturated water were then dried at 60°C for 30 minutes in a hot air oven. The FFA content of the dried samples was then determined by the titration method (AOCS method Ca 5a-40).

2.4.2 For continuous experiments, 50 mL samples were periodically collected from the output valve of reactor to a 250 mL glass bottle and immediately washed twice with warm water to stop the reaction and remove most of contaminants such as ethanol, gum and sulfuric acid. The washing step was repeated in a separatory funnel until the washing water had a pH of 7, let water separated about 15 minutes and finally water was drained out. The clean samples containing saturated water were then dried with household microwave setting at 360 W for 1.5 minutes; the saturated water was separated at bottom of a porcelain container. Repeat microwave drying again and let the sample cool down. The FFA content of the dried samples was then determined by the titration method (AOCS method Ca 5a-40).

2.5 Data analysis

2.5.1 FFA results were analyzed by level average analysis and based on the smaller-the-better principle (Peace, 1993). The analysis were performed as following:

2.5.1.1 Determine the mean for each experimental run. If it has only one data point for each experimental run, the mean response is the single data. As for the continuous experiments, two data points of 3RT and 4RT are used to calculate a mean response characteristic (y).

2.5.1.2 Calculate the mean response of each factor for each level, such as Cat1 = ($\sum y_{Cat1}$)/n, when n is number of response characteristics in that level.

2.5.1.3 Calculate the overall experiment average (T); $T = \sum y_i/n$, when y_i is a response characteristic.

2.5.1.4 Develop the response table and graph using the mean response.

2.5.1.5 Determine the effect of each factor, Delta = Max-Min.

2.5.1.6 Re-ordered significance of each factor by considering the Delta.

2.5.1.7 Select target levels of the significant factors that they will be used for a confirmation run.

2.5.1.8 Check interactions by plotting the maximum and minimum of each pair of factors. Such as interaction between Cat and Amp (CatxAmp), finding the maximum and minimum response in the response table; example for the preliminary experiment Cat2 and Amp3 obtained the maximum response, Cat4 and Amp1 obtained the minimum response then select their response characteristics to plot an interaction graph. If an interaction is detected, the intersection is shown. Perform the same fashion for each pair of the interactions.

2.5.1.9 Define the predicted FFA, using the prediction equation (μ); when μ = T – (Catx-T) + (Ampx-T) + (MRx-T) +… when x is a minimum response level in the response table and Cat, Amp, MR,…are the significant factors.

2.5.1.10 Conduct the confirmation run using target levels of the significant factors.

2.5.2 Energy consumption was measured in kWh with a watt-hour meter to compare with a theoretical consumption. Energy efficiency is defined as the actual consumption in Wh/kg CPO divides by the theoretical consumption and reported in percentage.