Appendices

Appendix A

Biodiesel Standards

Table A1 Comparison of different national standards for biodiesel

		Europe	**Austria**	**Germany**	**USA**	**Thailand**
Standard	Unit	EN	ON	DIN V	ASTM D-	Thai
Date		Sep	July	Sep 1997	Jan 2002	2006
Application		FAME	FAME	FAME	FAMAE	FAME
Density at 15°C	g/cm	0.86 -	0.85 -	0.875 -	-	860 to
Viscosity at 40°C	mm^2/s	3.5-5.0	3.5-5.0	3.5-5.0	1.9-6.0	3.5-5.0
Distillat. 95%	°C	-	-	-	90% @	<360
Flashpoint	°C	>101	>100	>110	>130	>120
CFPP (cold filter	°C	*country	0/-15	0/-10/-20	-	-
Sulfur	% mass	<10	<0.02	<0.01	<0.05	<0.0010
CCR 100%	% mass	-	<0.05	<0.05	-	-
10% dist. resid.	% mass	<0.3	-	-	-	<0.3
Sulfated ash	% mass	<0.02	<0.02	<0.03	<0.02	<0.02
Water	mg/kg	<500	-	<300	<0.05%	<500
Total contaminate	mg/kg	<24	-	<20	-	<24
Cu-Corros.	Number	1	-		<No.3	1
Oxidation	Hours	>6	-	-	-	>6
Cetane Number	Number	>51	>49	>49	>47	>51
Acid value	mgKOH/g	<0.5	<0.8	<0.5	<0.8	<0.5
Methanol	% mass	<0.20	<0.20	<0.3	-	<0.20
Ester content	% mass	>96.5	-	-	-	>96.5
Monoglyceride.	% mass	<0.8	-	<0.8	-	<0.80
Diglyceride	% mass	<0.2	-	<0.4	-	<0.20

		Europe	Austria	Germany	USA	Thailand
Triglyceride	% mass	<0.2	-	<0.4	-	<0.20
Free glycerol	% mass	<0.02	<0.02	<0.02	<0.02	<0.02
Total glycerol	% mass	<0.25	<0.24	<0.25	<0.24	<0.25
Iodine value	g	<120	<120	<115	-	<120
Linolenic acid	% mass	<12	-	-	-	<12
C18:3 and high.	% mass	-	<15	-	-	-
C(x:4) & greater	% mass	<1	-	-	-	-
Phosphor	mg/kg	<4	<20	<10	<0.001%	<10
Ramsbottom	% mass	-	-	-	0.1	-
Carbon residue	% mass	-	-	-	<0.050	
Gp I metals	mg/kg	<5	-	-	-	<5.0
Gp II metals	mg/kg	<5	-	-	-	<5.0
Alkalinity	mg/kg	-	-	<5	-	-

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Remark:

RME: Rapeseed oil methyl ester

FAME: Fatty acid methyl ester

VOME: Vegetable oil methyl ester

FAMAE: Fatty acid mono alkyl ester

Appendix B

Taguchi Methods

All contents in this appendix B are referred to (Peace, 1993).

1. Background

Dr. Genichi Taguchi's methods are a product of the Japanese post-World War II era. When resources were scarce and financial support was at best minimal, the demands for reconstruction of Japanese industry were enormous. Dr. Taguchi was born on January 1, 1924. His advanced formal training was directed toward textile engineering at Kiryu Technical Colledge, but he devoted extensive personal study to statistics. From an engineering background, Dr. Taguchi converted his study of statistics and advanced mathematics into a system merging statistical techniques and engineering expertise. The realities of deadlines and production limitations helped to shape his approach to apply experimental technique to actual design and production situations. This fostered a growing appreciation for taking assumptions for engineering knowledge to reduce the size of experiments and thereby speed up the experimentation process. He adapted the use of orthogonal array as an effective experimental design tool for greatly reducing the size of experiments while still achieving new insights and improving product designs and process productivity.

2. Determining the objectives

Developing a meaningful objective may require research on the part of the experimentation team. Retrieval of historical data, special tests or extra production runs may be needed. To determine the objectives, it needs many ways to achieve such as brainstorming, Pareto chart, process flow diagram, cause-and effect diagram, fault tree analysis, and failure made and effect analysis (FMEA) etc. By forming a foundation for understanding the process through the use of various techniques, the team can make an agreement on the objectives of the study and determine a relevant and meaningful quality characteristic for measuring success. The basic rules are:

2.1 Clearly define the objectives in terms that everyone on the team can understand.

2.2 Insure that all team members agree on and can support the objectives selected by majority of the team.

2.3 Attain mutual agreement on the criteria for measuring the ability to achieve the objectives.

2.4 Put into place communication safeguards to insure that all affected personnel become aware of any changes in the objectives or quality characteristic.

2.5 Provide the opportunity to respond to any changes so as to assure continued agreement and support by all team members.

2.6 Measurable characteristics are those end results that can be measured on a continuous scale such as dimensions, weight, pressure and clearance etc. Within the framework of measurable characteristics, it can be classified into nominal-the-best, smaller-the-better and larger-the-better characteristics. Nominal-the-best refers to a characteristic with a specific numerical goal or target value. A smaller-the-better characteristics is one in which the desire goal is to obtain a measure of zero such as machine wear, residue, percent contamination etc. A larger-the-better characteristics is opposite of a smaller-the-better characteristics is to achieve the highest value possible. Infinity is the ultimate objective. The examples of this characteristic are strength, shelf life, flash point and corrosion resistance etc.

3. Selecting the independent variables

After determining the team objectives and defining the quality characteristic, we will measure the ability to achieve our objective; we need to select the independent variables that have significant impact on this measurement. We can think of the quality characteristic as the dependent variable and each of the influences that affect it as an independent variable. The term factor is typically used instead of an independent variable. Normally, the tasks of selecting process variables (factors) and assigning appropriate factor level settings are the most time consuming and mentally exhausting part of the experiment planning. However, performing a thorough investigation of the potential factors affecting the selected quality characteristic will pay off in the long run. Careful selection of the process and product factors will help to uncover those effects that have significant influence on the end result. In generating

the list of potentially strong factors, the use of brainstorming is extremely valuable. In developing a list of factors, several approaches utilizing these tools may be considered. For example, the cause-and-effect diagram may be selected because it provides a systematic structure for creating the list of factors and it is easy to use and understand. Once the list of factors developed, the next step is to review each suggested factor and determine which factors should be incorporated into the study and which should be left for later consideration. The significant factors should be selected by discussion of the team members and set the agreement on those. This procedure is a screening the list of variables. Then factors classifying is needed by grouping into control and noise factors. The next step is to decide on the number of level of each factor and to specify the setting or value for each level. In defining appropriate levels for a particular control factor, you may learn that these values cannot in fact be controlled. Therefore, the factor needs to be redefined as a noise factor. The value or setting for another factor is held constant. In this case, the factor could be eliminated from further consideration in the particular study. Therefore, the process of screening the factors, classifies them as either control or noise factors and assigning value is actually an iterative process.

4. Experiment strategy

The majority of reasons to perform an experiment can be categorized into five major classifications.

4.1 Single experiment: to obtain a better understanding of how the process works, to know the important factors in a process. What causes changes in the end product?

4.2 Continuous experiment: to strive for continuous improvement, to reduce the variation by specific amount or down to a predetermined level.

4.3 Screening experiment: this process may have just been installed or may still be in the stages of being built. The process is sophisticated or very complex with many variables of potential importance. You are interested in refining the list of process factors down to a more manageable number in order to perform further experimentation to determine optimal settings for the most significant factors.

4.4 Focusing experiment: the experiment objective is specially targeted toward solving a problem. The purpose of the study is to determine the culprit or culprits by

studying simultaneous changes in the process and product variables. The advantage of this technique over other cause-and-effect tools occurs when the problem is sporadic and frequency of occurrence suggests that the problem is more likely to occur under a yet undetermined unique combination of process factor values.

4.5 Sequential experiment: this experiment is applicable where the process consists of many steps with numerous factors at each stage. The incorporation of all factors of interest into one experiment would result in a study too large to conduct practically. But by segmenting the process, a study of the first section can be performed first, followed by a second study involving the final portion of the process.

By determining which strategy best applies to our particular situation, we will be more capable properly planning the experiment and reducing the time needed to do so. Most important, the appropriate strategy will make the road smoother and easier and insure that we are able to achieve the objective.

5. Orthogonal arrays

The foundation for designing an experiment using Taguchi methodology is the orthogonal array. The orthogonal array is so efficient in obtaining only a relatively small amount of data and being able to translate it into meaningful and verifiable conclusion. Furthermore, the designs of experiments utilizing orthogonal arrays are basically simple to understand and the guidelines are easy to follow. Orthogonal means being balanced and not mixed. In the context of experimental matrices, orthogonal means statistically independent. If we examine a typical orthogonal array (Table B1), we will note that each level has an equal number of occurrences within each column.

Table B1 L_8 orthogonal array

$L_8(2^7)$							
No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**
1	1	1	1	1	1	1	1
2	1	1	1	2	2	2	2
3	1	2	2	1	1	2	2
4	1	2	2	2	2	1	1
5	2	1	2	1	2	1	2
6	2	1	2	2	1	2	1
7	2	2	1	1	2	2	1
8	2	2	1	2	1	1	2

Therefore, orthogonal arrays are much more cost effective and can provide more timely information.

5.1 Terminology

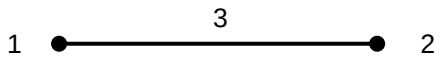
To facilitate the understanding of orthogonal arrays, it is essential to understand the standard nomenclature for describing each orthogonal array. Each array can be identified by the form $L_A(B^C)$. The subscript of L, which is designated by A, represents the number of experimental runs or combination of factors which can be conducted in the experiment. B denotes the number of levels within each column. The letter C, the exponential of letter B, identifies the number of columns available within the orthogonal array. orthogonal arrays are available with a variety of levels.

Analysis is based on combining the data associated with each level for each factor or interaction (column). The difference in the average results for each level is the measure of the effect of that factor. Those factors with the greatest effect or difference are the ones that can be used to improve the process and/or product.

6. Linear graphs

Assigning interactions at random to any available column within the orthogonal array can lead to incorrect analysis and faulty conclusions. To prevent the occurrence of these experimental design errors, Dr. Taguchi has developed a system for mapping interactions to the appropriate columns of the array. By setting up a graphical representation of the relationships among factors and the interactions between them, the experimenter can systematically assign factors (main effects) and interactions to the column within the orthogonal array without fear of confounding the effects of factors and their interactions. These graphical representations are called linear graphs.

Linear graphs are constructed of interconnecting dots or circles. Each dot or circle within a linear graph represents a column within the orthogonal array in which a factor can be assigned. The connecting line represents the interaction between the two factors represented by the dots at each end of line segment.



6.1 Assigning factors to linear graphs

The designing of the experiment can be easily accomplished in the following sequential steps.

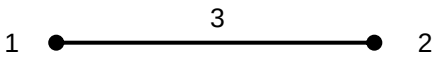
6.1.1 Select the orthogonal array. This step requires first calculating the total degrees of freedom needed foe studying the factors and interactions of interest. The degrees of freedom required are then matched against the degrees of freedom of the orthogonal arrays within the appropriate array series. The smallest array with at least as many degrees of freedom as required is selected.

6.1.2 Draw the required linear graph. Based on the factors and interactions identified for study in the planning phase, construct a linear graph. Use dots or circles to represent factors, and connect the dots with straight lines where interactions have been planned into the experiment.

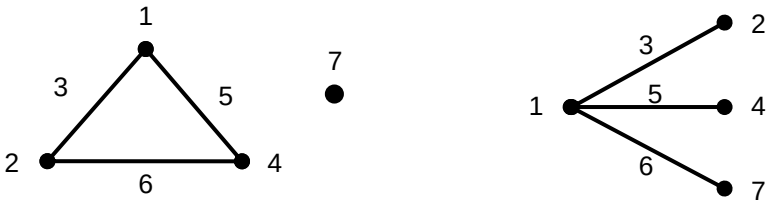
6.1.3 Match the required graph to a standard linear graph. Using Appendix B (Peace, 1993), compare the graph drawn in step 2 to the alternate shapes available for the orthogonal array selected. Select the standard linear graph that most closely resembles the graph drawn earlier.

Example of standard linear graphs for

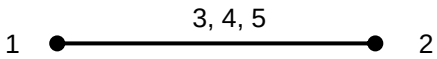
$L_4(2^3)$



$L_8(2^7)$



$L_{16}(4^5)$



6.1.4 Redraw the required linear graph. Based on the standard linear graph selected in step 3, modify the required graph to resemble the preferred graph from the appendix.

6.1.5 Assign factors and interactions. Mark each factor and interaction beside the appropriate dot or line segment. If a line segment of the linear graph will not be required to represent an interaction, that line may be used for assigning a factor.

6.1.6 Compare alternative mapping for the standard linear graph (if appropriate). If the orthogonal array selected has available more than one linear graph with the same identical shape, you can compare the potential column assignments from each of the graphs for your more expensive and hard to change factors. If the linear graph which appears more efficient is different from the one that you had previously selected, copy your modified linear graph, and renumber the dots and line segments as shown in the preferred linear graph pattern.

7. Preparing and conducting the experiments

7.1 Preparing the experiment.

Appropriate material and equipment must be used when conducting the experiment. Otherwise, the integrity of the experiment may be jeopardized and perhaps even violated. Therefore, it is important that required material and proper equipment are selected for completing each of the experimental runs.

If the purpose of the experiment is to make the process robust against differences in the incoming material, it is most essential that the material selected represent the full spectrum of material variability. For insuring robustness, only two levels, the opposing extremes, are typical required. The equipment to be used in conducting the experiment must be appropriate for the intent. Measuring something just to be obtaining data is like traveling without a destination and hoping that the road will take you somewhere meaningful. The primary factor in equipment selection is to provide a quantifiable measure tied directly to the objective of the experiment. That is the apparatus must be able effectively to obtain readings or measurements of the quality characteristic of interest. The precision of the instrument must be as good as or better than that desired for insuring a desired level of quality or variability.

7.2 Conducting the experiment

A valuable tool for coordinator is the experimental run sheet. This is a printout of the experimental run sequence with the corresponding setting or values for each factor in the experiment. The sheet can assist the coordinator in monitoring the progress of the experimental runs. The printout can serve as a checklist by which the operators mark off the setting change for each control factor as they go from the setup for one experimental run to the next.

8. Level average analysis

The type of analysis to be performed on the experiment data will be dictated by the design of the experiment. We can categorize the different designs in terms of the type of quality characteristic and the involvement of noise factors. When the quality characteristic has been defined in terms of a continuously measurable variable and no noise factors have been designed into the experiment, level average analysis may be the most appropriate technique for interpreting the data.

Level average analysis gets its name from determining the average response for factor and interaction levels and analyzing the importance of factors and interactions based on these computed values. The goal behind level average analysis is to identify the strongest effects and determine the combination of factors and interactions investigated that can produce the most desired result. The first step is to calculate the average experiment result for each level, factor and interaction (if defined in the experiment). The relative impact of each factor can be determined using either response table or graph. It is recommended that the analysis be performed both ways.

Using tabular method for analysis, a response table should be constructed displaying the average experiment result for each factor level under study. For each factor, the range in average response values should then be computed. In an experiment involving two level factors, this is merely the difference between the average values of two settings. However for three levels or more, you must identify the highest average response and the lowest average response. Be careful in identifying the proper levels for computing the range. The extreme values may not necessarily obtain from the highest and lowest factor settings. Once the differences have been ascertained, the next step is to separate the strong effects from the mild and weak effects. A sound and consistent approach is to rank the factors in order from the largest difference to the smallest. Then you will want to move from the largest to the smallest delta looking for a logical breaking point between the strong effects and the mild and weak effects. A rule of thumb is to identify approximately half of the effects as having a significant impact on the quality characteristic.

The strongest factors can also be identified graphically by plotting the average response value for each factor level; we can make relative comparisons of the slope between points plotted. Again, the factors can be ranked based on the relative steepness of the slopes. The rule of selecting approximately half of the factors investigated still applies. Once the strong effects and desired levels have been ascertained, a calculation of the predicted results is made based on the impact of the significant effects on the experiment results. Then the confirmation run is performed using the optimal factor level identified in the analysis. The results of the

confirmation run are compared against the predicted results to verify the analysis and confirm the assumptions made in designing the experiment.

If the interactions have been incorporated into the design of the experiment, analysis may become more detailed. Using the tabular method of analysis, the range for any interaction understudy is similarly compared to the ranges for each of the factors under study. If the interaction is not determined to be important based on the relative comparisons and logical breaking point, analysis of the interaction does not need to go any further. If on the other hand the interaction is deemed important, a matrix of the various combinations of the two factors comprising the interaction should be constructed. The levels of the associated factors can be selected on the basis of the factor level combination resulting in the most desired experiment result.

Graphical analysis also can be even more helpful in determining the best combination of interacting factors. The slope of the interaction is compared to the slope of each of the factors or main effects. As in tabular analysis, if the interaction is not considered important, we do not need to go any further. If the interaction is determined to have a strong effect, we will then need to construct an additional graph comprised of points representing the average response for each combination of interacting factors. The recommended factor levels are then selected based on the preferred point on the graph. The advantage of developing an interaction graph is that not only can you determine the most desired point, but the strength of the interaction is often clearer when shown graphically.

The analysis strategy will change depending on the type of quality characteristic. If the output of interest is a larger-the-better characteristic, the emphasis will be on determining which levels result in the highest response. For a smaller-the-better characteristic, the goal is to identify those factor levels that will achieve the lowest expected results. For nominal-the-best quality characteristics, the analysis is more complicated. Moving the average process results closer to the desired or target value is hardly desirable if the variation from one unit or batch to the next increases. Therefore, regular analysis is not recommended for handling nominal-the-best quality characteristics. A preferred approach is to run repetitions for each experimental run and to treat the repetitions as noise factor setting combinations.

Once the confirmation run has been performed, the actual and predicted results can be compared against each other. If the results are similar, then the experiment can be deemed a success, and preferred settings should be instituted. If the confirmation run results are disappointing, the team will need to return to the planning phase to reevaluate the elements that went into the experiment. A possible cause is the omission of a key factor from the experiment. Perhaps a powerful interaction was not considered. Another common cause is the setting of factor levels too close together for the experiment. In these situations, the factor is found insignificant during the analysis and is not accounted for in the validation. During the confirmation run, this factor operates at a value beyond the experimental values. Although the factor is not a strong effect within the experiment range, moving outside the region cause a significant change in the output of interest. Therefore, the results are different from what was predicted. Another potential problem occurs when randomization is used to conduct the experiment. After performing the experiment with the order of experimental run scrambled, the team fails to reorder the sequence of the runs for the analysis. If the confirmation run results are not as good as the predicted results, but better than the current production results, you may want to consider implementing the recommended settings temporarily while returning the planning phase. This at least gives you some improvement until better understanding of the process or product can lead to a better confirmation run and more desirable results.

Appendix C

Interaction Graphs and Temperature Profiles

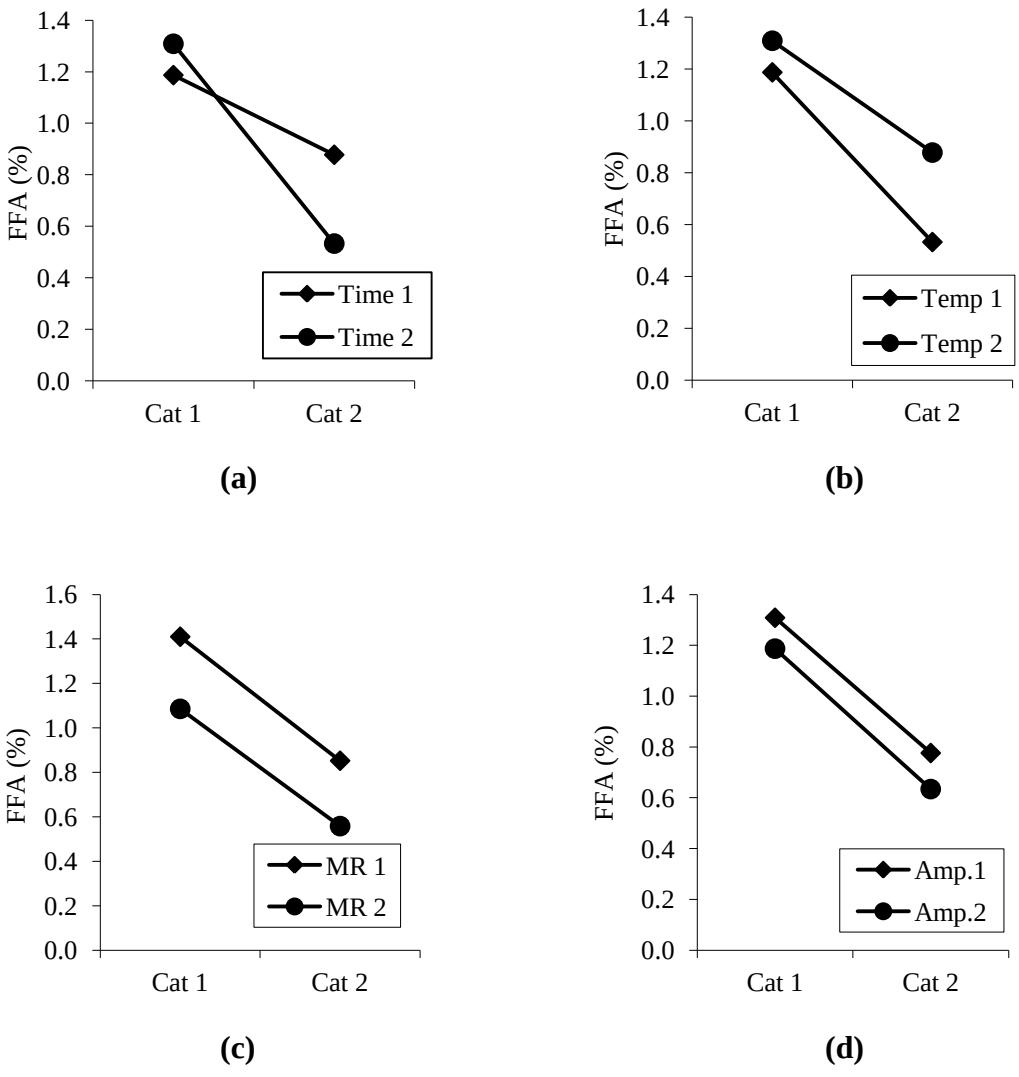
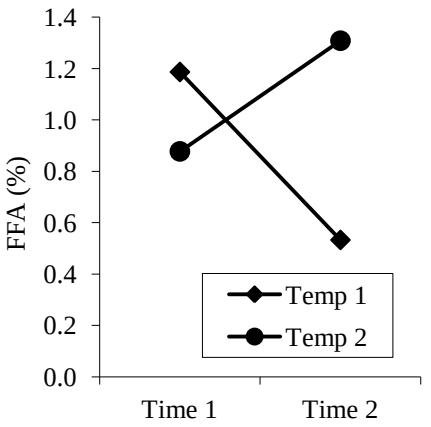
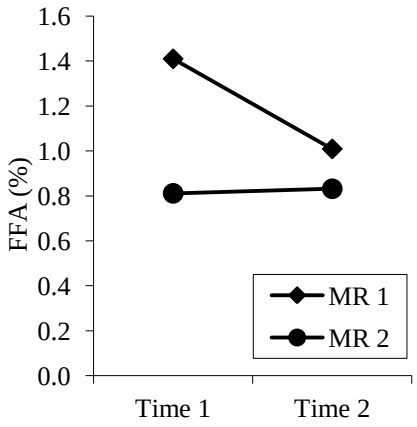


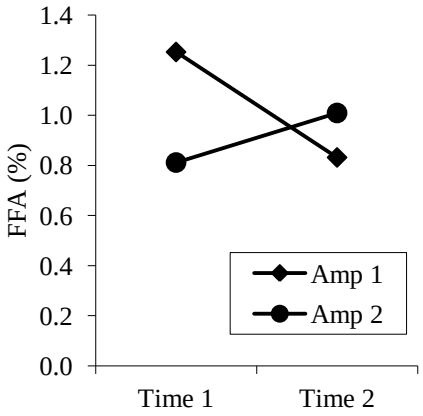
Figure C1 Interaction graphs between Cat-Time (a), Cat-Temp (b), Cat-MR (c) and Cat-Amp (d) of the secondary experiments



(a)

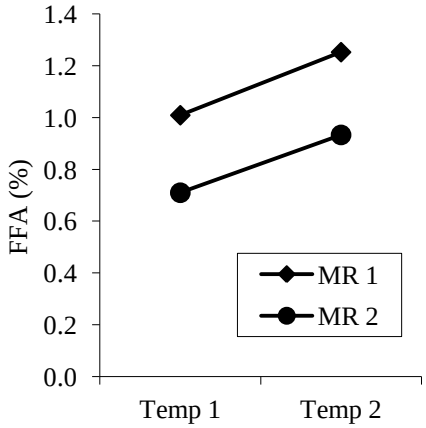


(b)

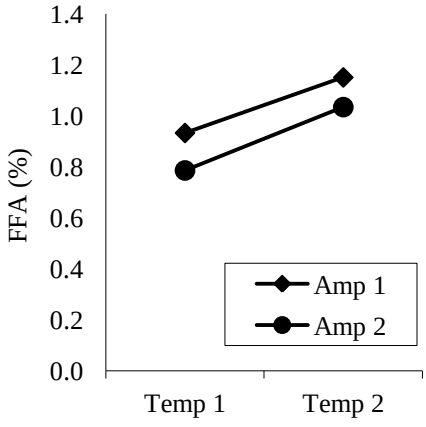


(c)

Figure C2 Interaction graphs between Time-Temp (a), Time-MR (b) and Time-Amp (c) of the secondary experiments



(a)



(b)

Figure C3 Interaction graphs of between Temp-MR (a) and Temp-Amp (b) of the secondary experiments

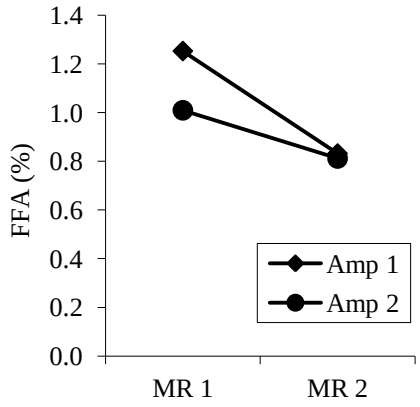
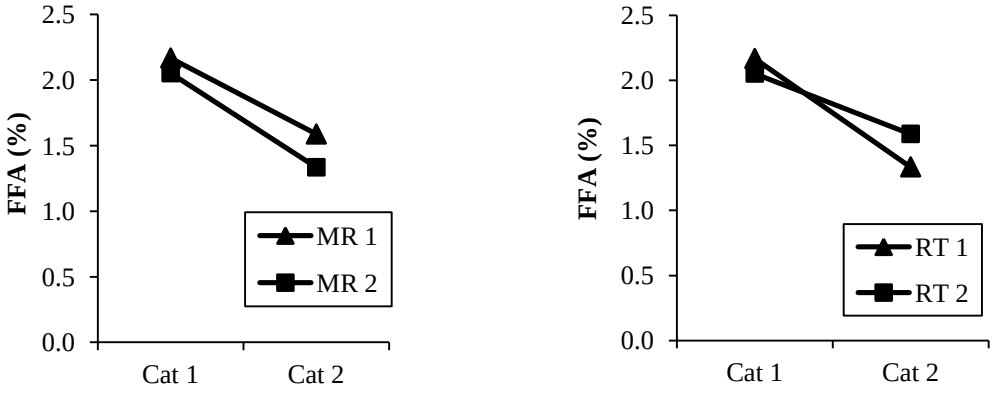


Figure C4 The interaction graph between MR-Amp of the secondary experiments



(a) (b)

Figure C5 Interaction graphs between Cat-MR (a) and Cat-RT (b) of the 2nd continuous experiments

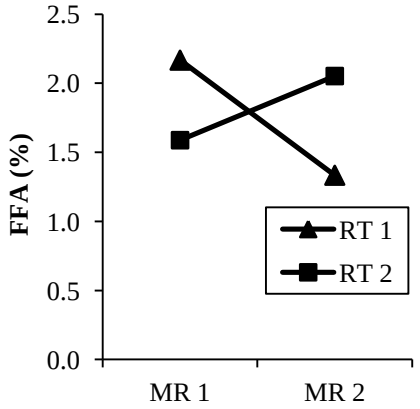
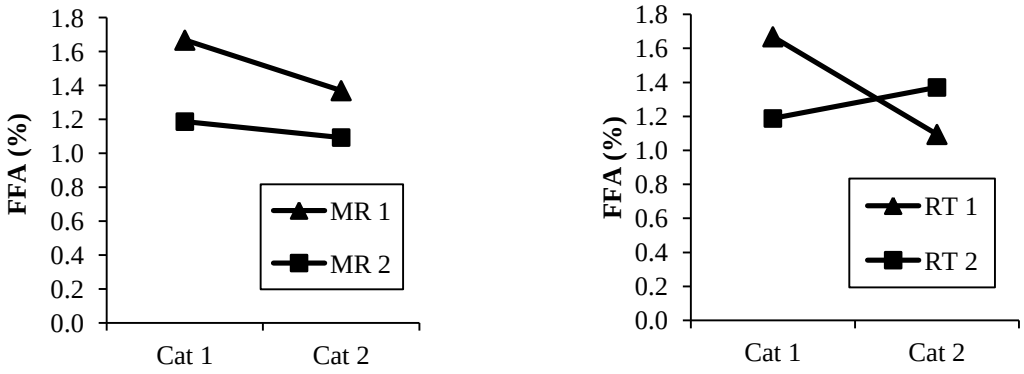


Figure C6 The interaction graph between MR-RT of the 2nd continuous experiments



(a) (b)

Figure C7 Interaction graphs between Cat-MR (a) and Cat-RT (b) of the 3rd continuous experiments

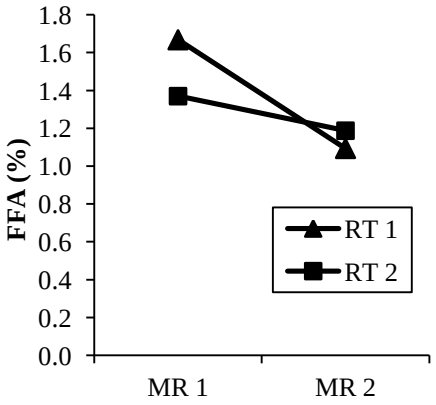
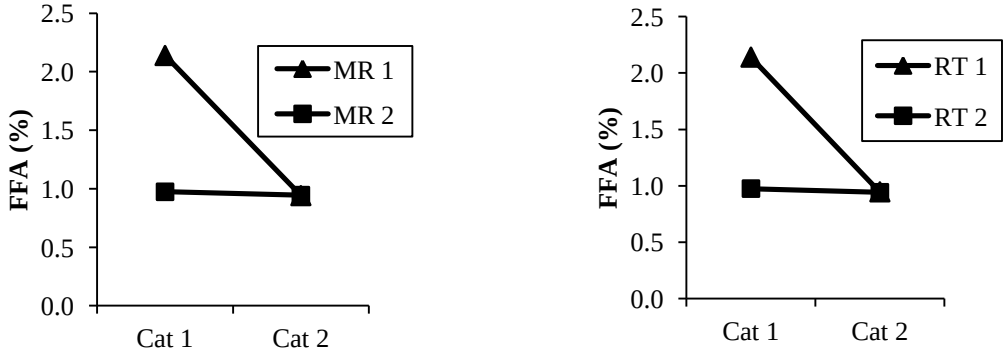


Figure C8 The interaction graph between MR-RT of the 3rd continuous experiments



(a) (b)

Figure C9 Interaction graphs between Cat-MR (a) and Cat-RT (b) of the 4th continuous experiments

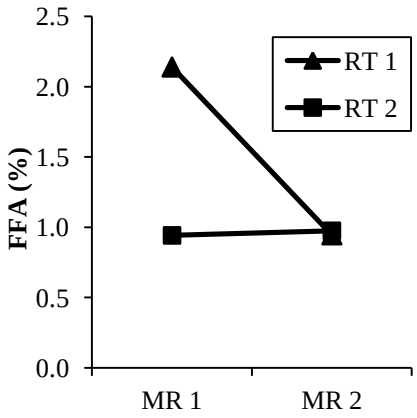
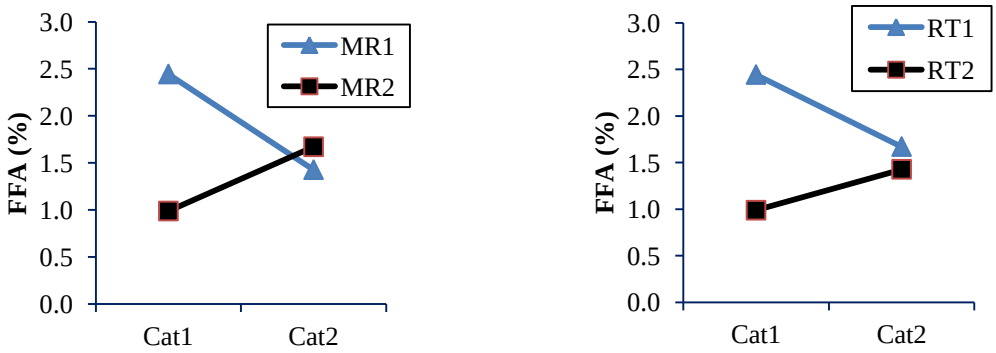


Figure C10 The interaction graph between MR-RT of the 4th continuous experiments



(a) (b)

Figure C11 Interaction graphs between Cat-MR (a) and Cat-RT (b) of the CSTR experiments

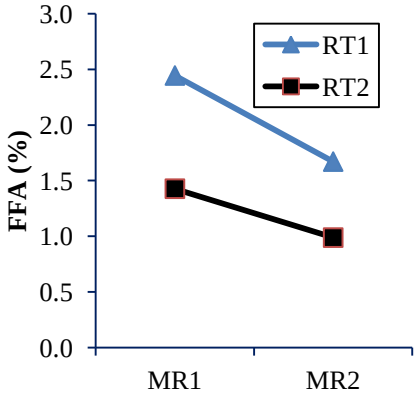


Figure C12 The interaction graph between MR-RT of the CSTR experiments

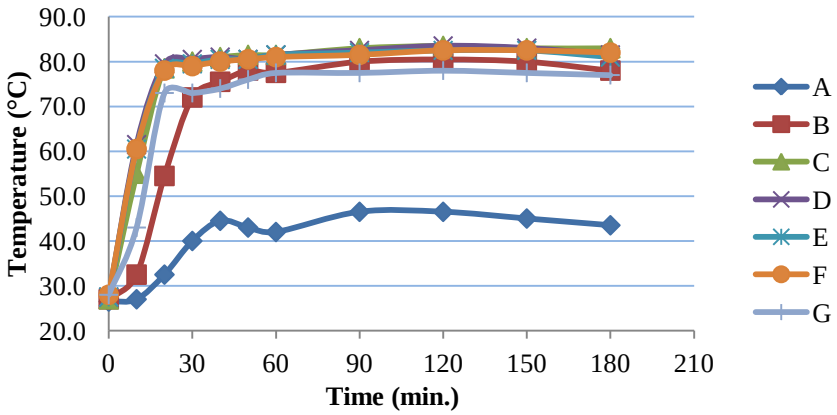


Figure C13 Reactor temperature profile: Run # 1 of the 2nd continuous experiments

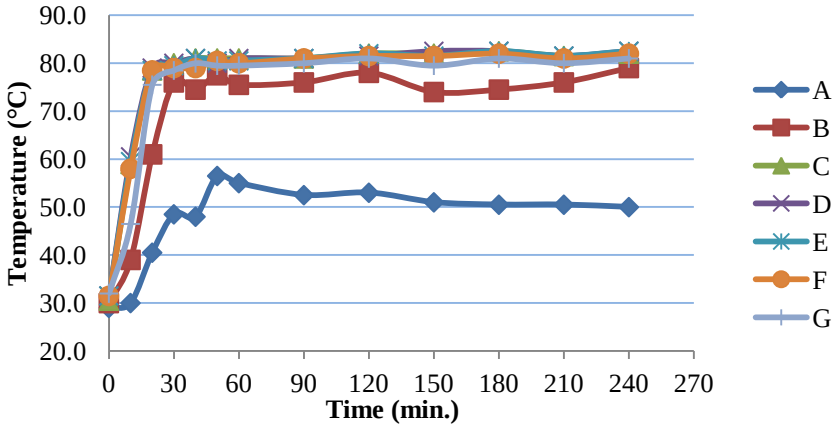


Figure C14 Reactor temperature profile: Run # 2 of the 2nd continuous experiments

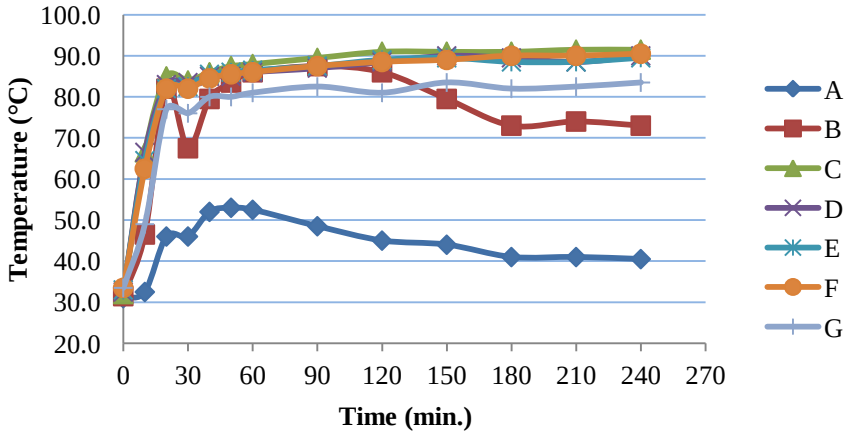


Figure C15 Reactor temperature profile: Run # 3 of the 2nd continuous experiments

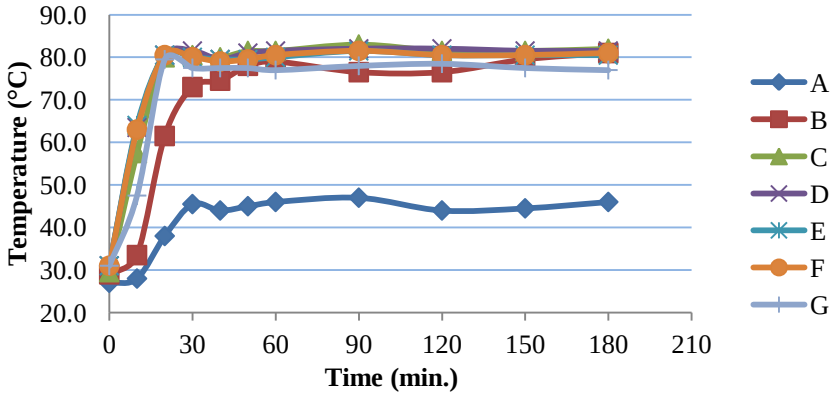


Figure C16 Reactor temperature profile: Run # 4 of the 2nd continuous experiments

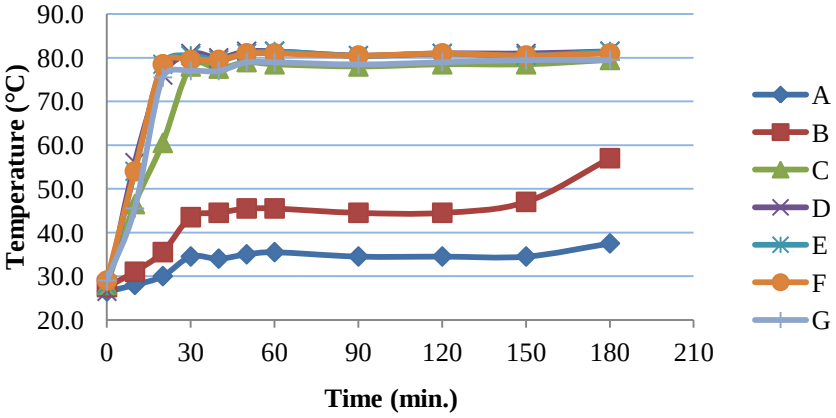


Figure C17 Reactor temperature profile: Run # 5 of the 2nd continuous experiments

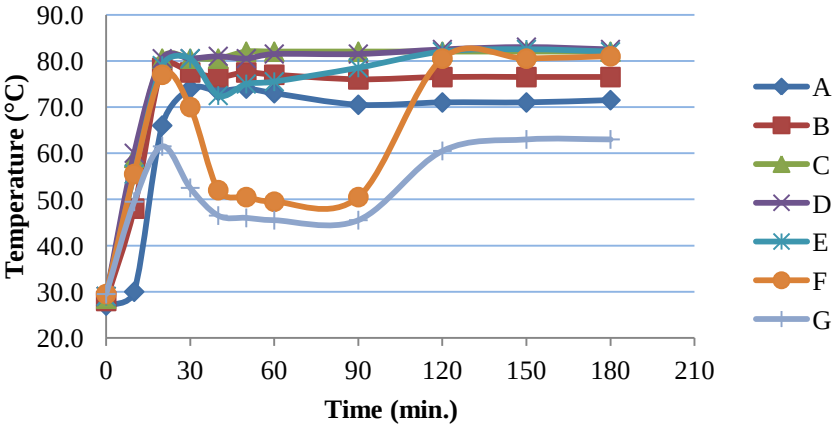


Figure C18 Reactor temperature profile: Run # 1 of the 3rd continuous experiments

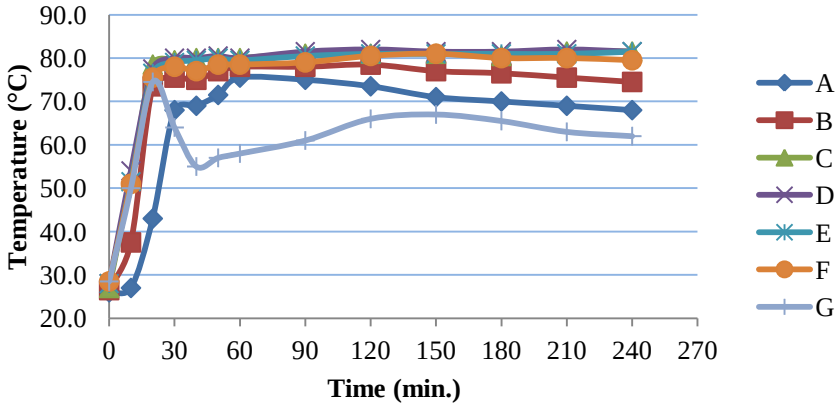


Figure C19 Reactor temperature profile: Run # 2 of the 3rd continuous experiments

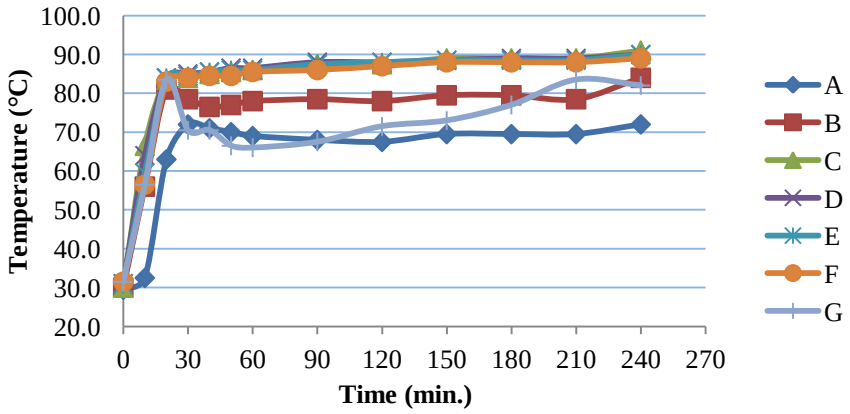


Figure C20 Reactor temperature profile: Run # 3 of the 3rd continuous experiments

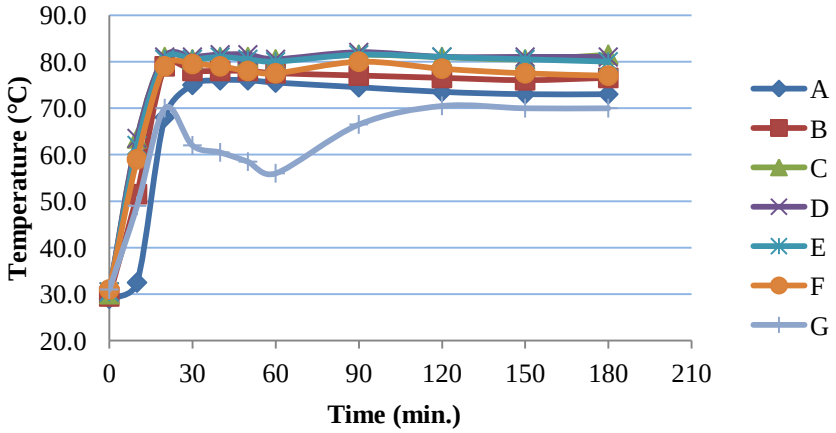


Figure C21 Reactor temperature profile: Run # 4 of the 3rd continuous experiments

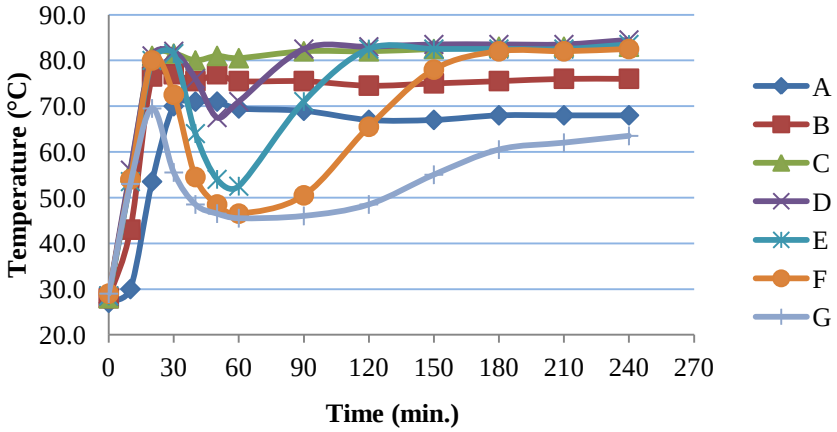


Figure C22 Reactor temperature profile: Run # 5 of the 3rd continuous experiments

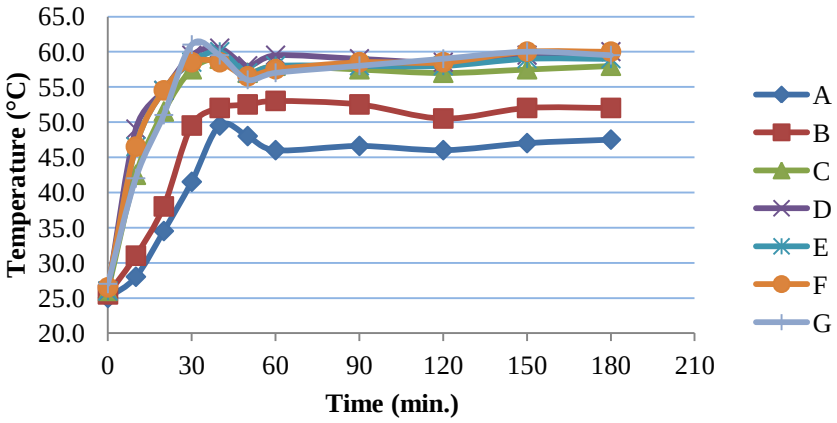


Figure C23 Reactor temperature profile: Run # 1 of the 4th continuous experiments

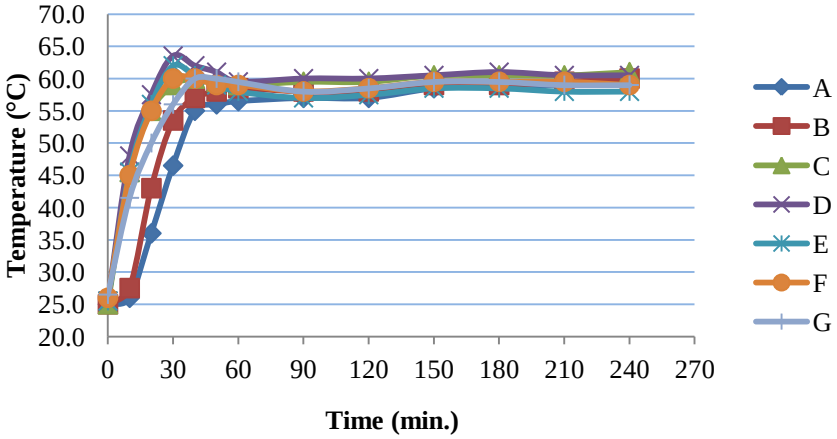


Figure C24 Reactor temperature profile: Run # 2 of the 4th continuous experiments

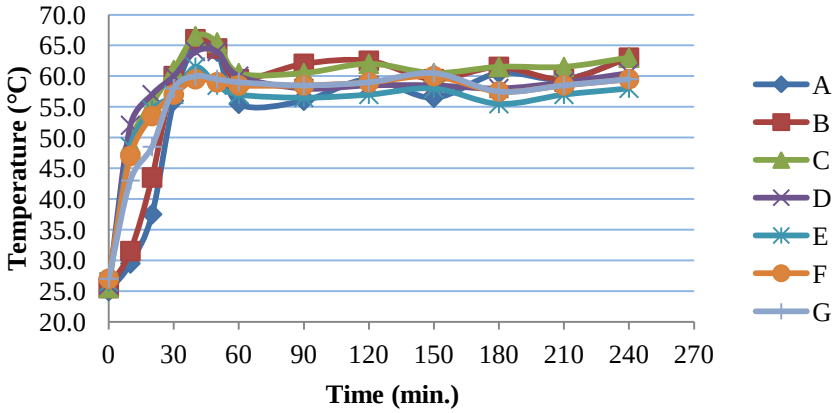


Figure C25 Reactor temperature profile: Run # 3 of the 4th continuous experiments

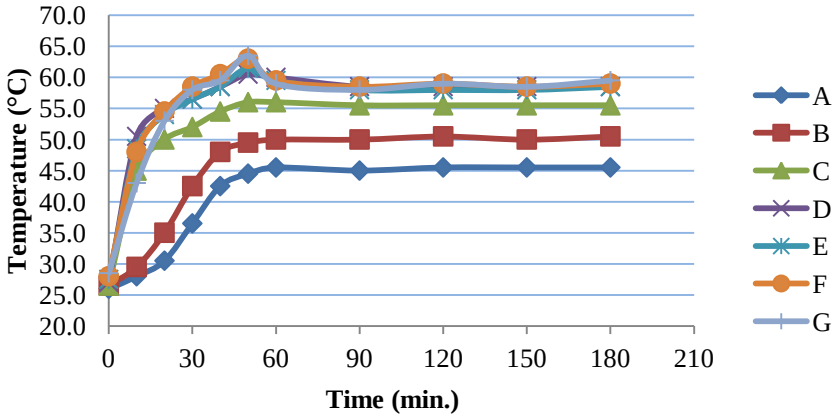


Figure C26 Reactor temperature profile: Run # 4 of the 4th continuous experiments

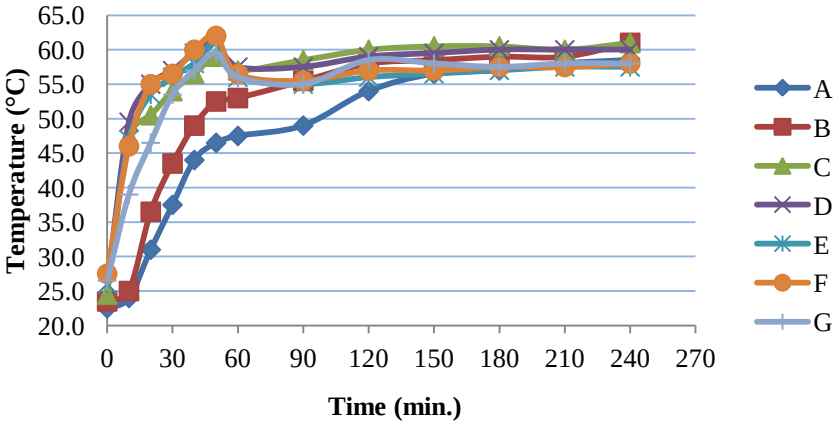


Figure C27 Reactor temperature profile: Run # 5 of the 4th continuous experiments

Appendix D

CSTR Drawing

A continuous stirred-tank reactor drawings are illustrated.

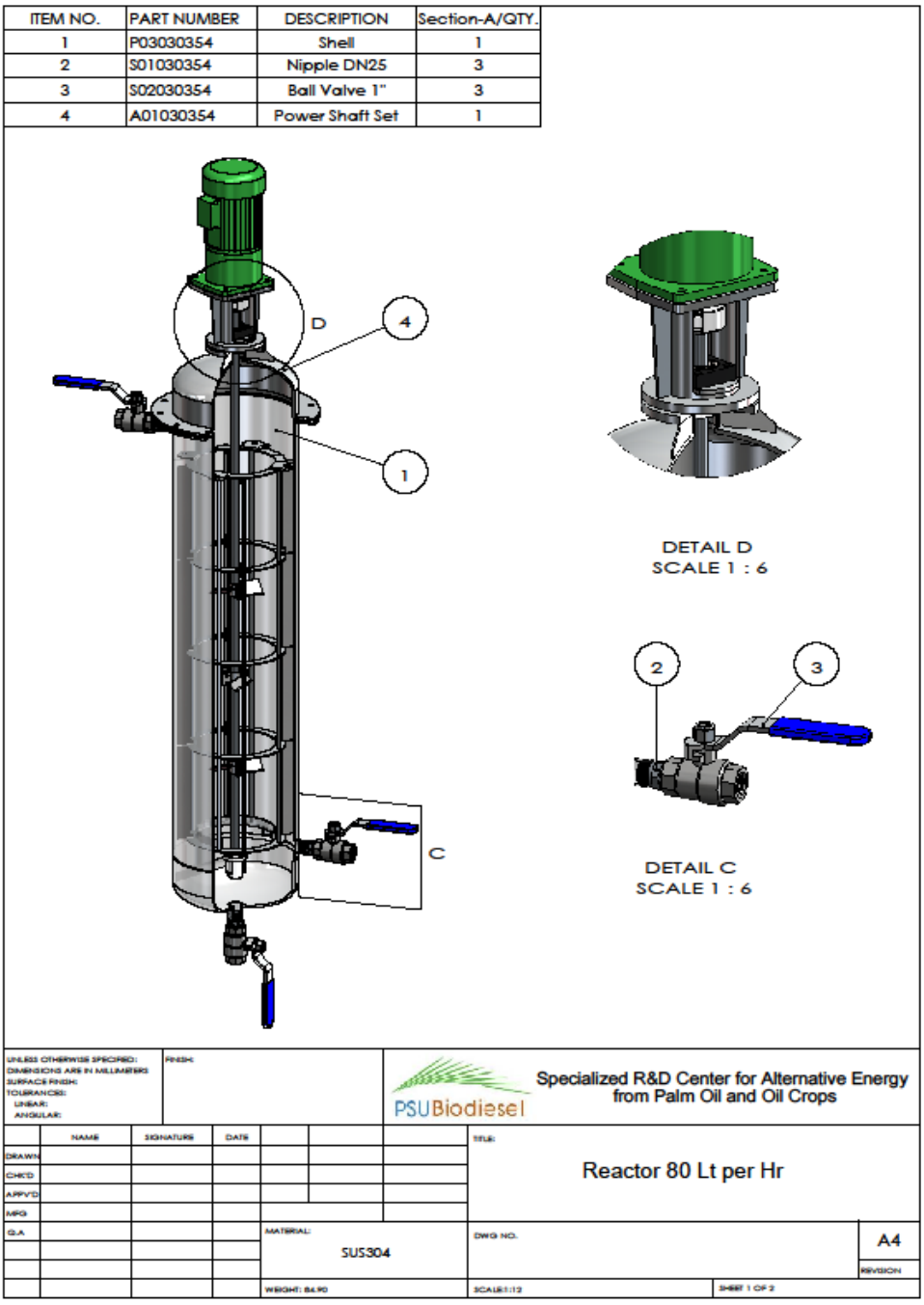


Figure D1 The overview of a CSTR for continuous esterification.

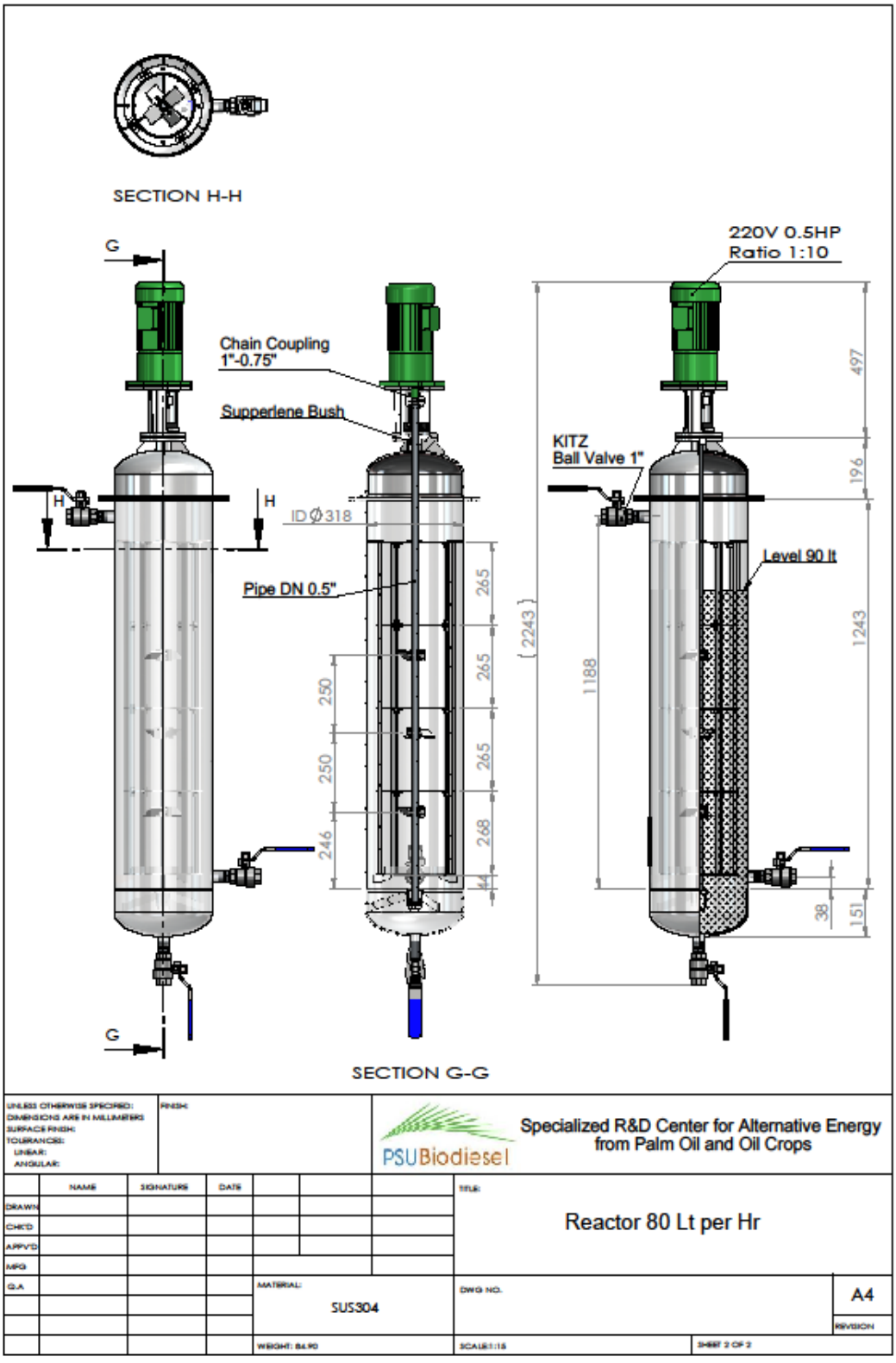


Figure D2 The details of a CSTR for continuous esterification.

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Patent Pending

Petty patent: Chakrit Tongurai and Thanet Waisuwan. 2012 Continuous Palm Fruit Frying for Palm Oil Mill. No.1203000082. Thailand Patent Office.

List of Publication and Proceedings

Thanet Waisuwan, Sutham Sukmanee and Chakrit Tongurai. 2011. Batch Process Esterification of Crude Palm Oil with Ethanol Assisted under Ultrasonic Irradiation. The 2011 International Conference on Alternative Energy in Developing Countries and Emerging Econimies (2011 AEDCEE), 25-28 May 2011, J.B. Hotel Hatyai, Thailand.