

**NON-CATALYTIC AND SOLVENT-FREE ESTERIFICATION OF ACETIC ACID  
WITH ETHANOL USING COILED FLOW INVERTER FOR ETHYL ETHANOATE  
SYNTHESIS IN FOOD INDUSTRY**

by

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## LIST OF SYMBOLS

Symbol	Description	Unit
$\lambda$	Curvature ratio	1
Re	Reynold Number	1
$\rho$	Density of fluid	kg/m <sup>3</sup>
$u$	Velocity of fluid	m/s
$d$	Inner diameter of tube	mm
$\mu$	Viscosity of fluid	Pa.s or N.s/m <sup>2</sup>
$Q$	Volumetric flow rate	mL/min
A	Cross section area of tube	m <sup>2</sup>
RT	Residence time	min
V	Volume of tube	m <sup>3</sup>
$k_f$	Forward rate constant	L/(mol.min)
$C_{Ao}$	Initial concentration of acetic acid	mol/L
$C_A$ and [A]	Concentration of unreacted acetic acid	mol/L
Dc	Diameter of coil	mm
Dt	Inner diameter of tube	mm

## LIST OF ABBREVIATIONS

Symbol	Description
CFI	Coiled flow inverter
CFD	Computational fluid dynamics
COMSOL	Computational fluid dynamics software
USD	United States Dollar
ILs	Ionic liquids
RD	Reactive distillation
PEF	Pulsed electric field
ATRP	Atom transfer radical polymerization
PDMAEMA	Linear and branched 2-(dimethylamino)ethyl methacrylate
RTD	Residence time distribution
ACCFI	Asymmetrical compact coiled flow inverter
SCCFI	Symmetrical compact coiled flow inverter
CCFI	Compact coiled flow inverter
2D	Two-dimensional
3D	Three-dimensional
ANSYS	A computational fluid dynamics software
PTFE	Polytetrafluoroethylene
S	Indicates reaction set in very low laminar Reynold Number
F	Indicates reaction set in high laminar Reynold Number
SDGs	Sustainable Goal Developments

**PENGESTERAN TANPA PEMANGKIN DAN BEBAS PELARUT DENGAN  
ETANOL DENGAN MENGGUNAKAN PENYONGSANG ALIRAN BERGELUNG  
UNTUK SINTESIS ETIL ETANOAT DALAM INDUSTRI MAKANAN**

**ABSTRAK**

Pengesteran etanol dan asid asetik tanpa pemangkin dan bebas pelarut telah dijalankan dalam peralatan intensif baru, penyongsang aliran bergelung (CFI) untuk mengkaji keupayaan CFI dalam mendapatkan jumlah etil etanoat yang lebih tinggi dalam masa yang lebih singkat. Kajian eksperimen dilakukan untuk nombor Reynold ( $Re$ ) laminar yang sangat rendah bervariasi dari 0.26 hingga 0.51 dan 25 hingga 75 untuk  $Re$  laminar yang tinggi pada nisbah isipadu molar 3: 1 etanol ke asid asetik dan suhu tetap 80 °C. Kesan penggunaan  $Re$  yang berbeza terhadap penukaran asid dan kepekatan etil etanoat dikaji. Profil pencampuran bahan tindak balas dalam keadaan aliran laminar disahkan dalam COMSOL Multiphysics 5.5 manakala kesan perubahan dua parameter CFI sama ada diameter dalaman tiub atau diameter gegelung, disiasat melalui analisis pengiraan dinamik bendalir (CFD) di dalam COMSOL. Hasil eksperimen menunjukkan bahawa pada keadaan  $Re$  laminar yang sangat rendah, penukaran tinggi (> 80%) etil etanoat dapat diperoleh ketika  $Re$  menurun mendekati 0. Namun, penukaran sederhana (> 75%) dapat dicapai pada waktu yang lebih pendek ketika  $Re$  meningkat pada keadaan  $Re$  laminar tinggi kerana pencampuran perolakan yang cekap yang terbentuk dalam CFI pada kadar aliran tinggi. Telah diperhatikan juga bahawa diameter gegelung yang lebih kecil menghasilkan lebih banyak penyongsangan aliran manakala diameter dalaman tiub yang lebih kecil mendorong kecekapan aliran pencampuran yang lebih tinggi di dalam tiub. Diameter gegelung dan diameter dalaman tiub yang optimum sangat penting untuk diketahui kerana ia dapat meningkatkan kecekapan pencampuran dan kepekatan produk untuk memproses etil etanoat pada waktu yang lebih singkat untuk industri makanan.

# **NON-CATALYTIC AND SOLVENT-FREE ESTERIFICATION OF ACETIC ACID WITH ETHANOL USING COILED FLOW INVERTER FOR ETHYL ETHANOATE SYNTHESIS IN FOOD INDUSTRY**

## **ABSTRACT**

Non-catalyzed and solvent-free esterification of ethanol and acetic acid has been conducted in a novel intensified equipment, coiled flow inverter (CFI) to study the mixing performance of CFI in obtaining higher amount of ethyl ethanoate in a shorter time. The experimental study was carried out for very low laminar Reynold Number ( $Re$ ) varies from 0.26 to 0.51 and for high laminar  $Re$  starting from 25 to 75 at constant volume ratio 3 : 1 of ethanol to acetic acid and at constant temperature 80°C. The effects of applying different  $Re$  towards the acid conversion and ethyl ethanoate concentration were examined. The mixing profile of fluids in laminar flow conditions were validated in COMSOL Multiphysics 5.5 while the aftermath of changing two CFI parameters either internal diameter of tube or coil diameter, was investigated via computational fluid dynamics (CFD) analysis in COMSOL. The experimental results showed that at very low laminar  $Re$  condition, high conversion ( $> 80\%$ ) of ethyl ethanoate can be obtained as the  $Re$  decreased approaching 0. However, moderate conversion ( $> 75\%$ ) was attained at shorter time when  $Re$  increased in high laminar  $Re$  condition due to efficient convective mixing created in CFI at high flow rates. It was also observed that smaller diameter of coil able to create more flow inversions while smaller inner diameter of tube promotes greater mixing flow efficiency in the tube. Optimum diameter of coil and tube inner diameter are crucial to be known as it can promote higher mixing efficiency and product concentration for processing ethyl ethanoate at shorter time for food industry.

# CHAPTER 1

## INTRODUCTION

This chapter presents the background of the research area and the prominence of using coiled flow inverter for ethyl ethanoate synthesis through esterification of ethanol and acetic acid. It also covers problem statement, main purposes of conducting this final year project and scope of study.

### 1.0 Research Background

Food is essential for all living things in the world. Not only human needs food the most, animals and even plants need food and nutrients to stay alive. Nutritious food keeps us healthy, active and strong. It is also the main source of energy for all living things and helps their growth. Food can be manufactured from plants, fruits and animals such as chicken and fish. Thus, food processing are required to transform these agricultural and raw products into the desired food with longer shelf life (Ghoshal, 2018). It modifies the taste, texture and aroma of food to increase the aesthetic properties and foods nutritional values.

Therefore, food industries have its foothold in every country to produce abundance of food sources and making variety of food that meets the demands of human and other living creatures. Food harvesting, processing, packaging, production deliverables facilities, distribution and also food disposal are categorized under food industry. It is not only responsible for food processing, but it will also focus on food safety, food security, public health, social development and food nutrition as well (Sadiku et al., June 2019). Apart from that, production of food derivatives is classified under food industry since it gives significant impacts to the flavour, aroma, sweetness of food and human health.

Food derivatives come from several sources which are meat and animal derivatives, plant derivatives, fruit-derived products and food derivation from hydrocarbon. Animal and meat derivatives are described as all parts of the slaughtered warm-blooded land animals that are cut off carefully via a treatment and every carcass warm-blooded land animals' products

and their derivatives (European Pet Food Industry Federation (FEDIAF), 2011). Cat, fish, dog food are the examples of animal and meat derivatives as they are processed from slaughtered and carcasses of animals' parts. Plants also can be derived to get beneficial extracted nutrition or chemical substances. For instance, polyphenols that are available in nuts, soy, grapes, vegetables and other food which function as antioxidant and able to give good impacts to our health such as improving our skin, digestive and cardiovascular systems (Xia et al., 2010). Fruits also can be processed, cut, and separated to get fruit by-products like citrus pulp, citrus juice and citrus purees that can be used to improve the aroma and sweetness of other food products. Besides that, several food substances from hydrocarbon derivatives are created whenever a functional group or other elements replaces the hydrogen atoms in the original hydrocarbon. For example, ethane becomes ethanol due to the replacement of hydrogen with oxygen-hydrogen (OH) group (Campbell et al., 2018). In this case, ethanol is the hydrocarbon derivative from ethane. Other example of hydrocarbon derivatives that can become food derivatives is ethyl ethanoate.

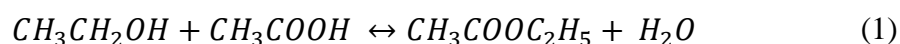
Ethyl ethanoate or its common name, ethyl acetate is one of the important food processing materials which frequently utilized in food and beverages industry. It is an organic compound and presents as colourless liquid with slightly fruity smell (Barnes, 2018). It will not cause harm as long as it is being processed carefully and food manufacturers follow strictly permitted amount of food additives to be added in food. Permitted food additives and their maximum limits in food are listed in Part V and schedules in Malaysia Food Act (1983) and Food Regulations (1985). It might be toxic to human if the pure ethyl ethanoate is directly inhaled or ingested. Since it can be considered as natural as long as no direct exposure towards human, many industries utilized the existence of ethyl ethanoate in their processes.

Pharmaceutical, food and beverages industries still use ethyl ethanoate as a solvent, extraction medium, flavours and a driver to increase the food aroma. Sometimes, it is run as

solvent to extract a desired substance from plants or food, for instance, tobacco is extracted from decaffeinated coffee with the assistance of ethyl ethanoate. Other than that, it is synthesized to upgrade the fruity flavour in wines and added as artificial flavour in ice cream, confectionery, candies, cakes and artificial fruit essences (Technavio, 2020). Due to its great functionalities in food and beverages, it is highly demanded by food industries to produce ethyl ethanoate continuously with higher yield of production. Thus, this leads to successful and growth of ethyl ethanoate market globally.

Apparently, the Asia Pacific has been firmly held the title as the largest producer and exporter of ethyl ethanoate since it is the largest supplier of ethyl ethanoate that able to fulfilled almost 80% of global ethyl ethanoate demand (ICICI Securities Retail Research, March 2021). In 2020, almost 4 million metric tons of ethyl ethanoate were demanded by the consumers from all over the world. It is forecasted that the global ethyl ethanoate market demand will rapidly increase and achieve USD 5.47 billion in 2027 (Data, 2020). This is due to rising demand of ethyl ethanoate for paints, coatings, food and beverages especially in China, India, Indonesia and Singapore. Most of the manufacturers create ethyl ethanoate synthetically by undergoing a chemical reaction.

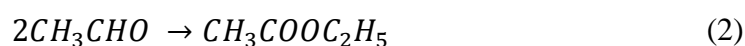
In food industry, ethyl ethanoate production can be done via three chemical processes. The first method is via Fischer esterification process of ethanol and acetic acid with presence of acid catalyst such as concentrated sulphuric acid and hydrochloric acid (Pattanaik and Mandalia, 2011). Usually, this reaction process will yield 65% of ethyl ethanoate at room temperature. The chemical reaction equation is shown as below :



The acid catalyst will be added to remove the water and make the equilibrium shifted to the right. Following the Le Chatelier's principle, forward path reaction will be more

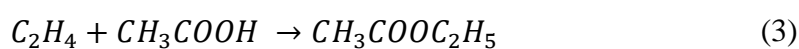
favourable with lower amount of water produced during the mixing. This reaction is reversible and exothermic as well. This method is mainly used in industry because its reaction rates is higher than other method (Santaella et al., 2015). Homogeneous catalysts are still being applied in food production because it increases the product selectivity and has wider accessibility towards all active sites. However, considering environmental issues and unstable economy nowadays, it is not suitable to be used in food as it may cause equipment corrosion, more solid wastes and toxics will be generated (He et al., 2014). Moreover, it is difficult to handle the homogeneous catalyst especially in separating them from the system and causes higher cost of manufacturing and maintenance.

The second reaction that can produce ethyl ethanoate is the Tishchenko Reaction of acetaldehyde by aluminium triethoxide which is the catalyst used in this reaction (Pattanaik and Mandalia, 2011) . This reaction usually used by companies in German and Japan. The chemical equation of the reaction is written as below :



There are two different pathways available for this reaction. The first pathway is by going through dehydrogenative process with palladium-based catalyst or copper as the catalyst. It will produce ethyl acetate, hydrogen and few by-products that causes purification process of ethyl ethanoate becomes more expensive. The second pathway is more towards oxidation which utilizes palladium (II) oxide (PdO) supported catalyst.

Lastly, the third route to produce ethyl ethanoate is by adding acetic acid to ethylene with heteropoly acid and clay as the catalyst. The chemical reaction process is as below :





Although this reaction has been commercialized within industry, the percentage yield of the products did not improve much. It is because conventional methods of esterification used will generate side reaction such as oxidation, the equipment might corrode and longer time of reaction (He et al., 2014). Adding acetic acid to ethylene also require additional tanks and apparatus which requires bigger size of production plant, and this will lead to higher capital and operating costs. In fact, the reaction slowly becomes difficult to be handled due to formation of acetaldehyde in between the reaction.

Therefore, in this present study, unpopular alternative but safe to apply, that is non-catalytic and free-solvent esterification reaction involving ethanol and acetic acid in novel process-intensifying equipment called coiled flow inverter (CFI) will be discussed further to observe its performance in synthesizing ethyl ethanoate for food industry.

## **1.1 Problem Statement**

In order to conform to the global market demand, it is crucial to have efficient production process of ethyl ethanoate with higher conversion and yield. Even though Fischer esterification method is still being used in industry due to its simplest reaction and wide availability of all reactants, the equilibrium conversion of the reaction is lower which is about 64% (Santaella et al., 2015) and yield 65% of ethyl ethanoate at the end of the process (Pattanaik and Mandalia, 2011). Usually in industrial process, this reaction method takes place in a reactor or vessel and further purified in a distillation column as shown in Figure 1.1. The ethanol and acetic acid will be fed into the reactor with acid catalyst at elevated temperature like 80°C. Even though some reactors have stirrer, the mass transfer between the reacting phases still slower due to bigger size of reactor which leads to inefficient mixing in batch reactor. It will take longer time for the reactants to completely mix between them and contribute to lower product yield even at higher residence time.

Using excess acid or alcohol is suggested in order to improve the ethanol and acetic acid conversion and ethyl ethanoate yield (Santaella et al., 2015). However, if ethanol is being mixed with acetic acid excessively, it will affect purification process in distillation column as the ternary separation of ethanol-acetic acid-water becomes more difficult due to azeotrope formed between these components. If excess acid is used in this esterification reaction, it will cause isomerization or dehydrate the alcohol (Blanchard and Brennecke, 2001). In fact, acids are corrosive and hazardous. Having excess acid as the catalyst will only create more harm than good especially when considering the challenges to dispose the acidic waste. The water generated from the process also need to be treated properly before discarding them to the environment. Preserving the environment is significant despite the urgency of maximizing the production rate as demanded by the consumers. Moreover, separation of acetic acid from water becomes more complicated and needs additional equipment like entrainer to solve this matter (Santaella et al., 2015). However, adding other equipment will increase the overall cost of process including equipment and maintenance cost.

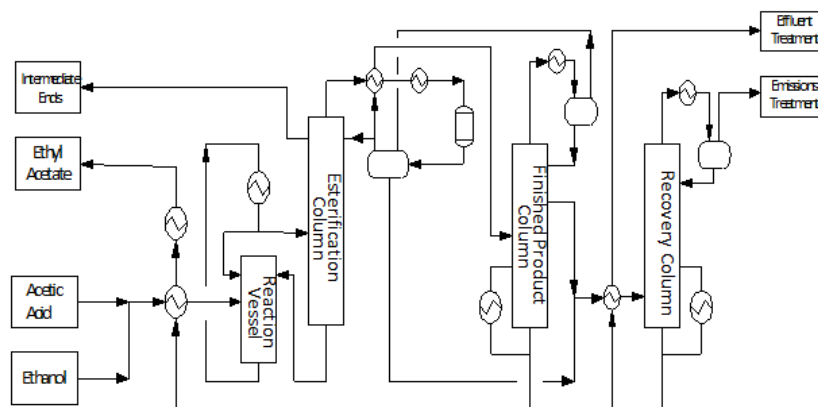


Figure 1.1 Process block diagram of ethyl ethanoate production in food processing industry (Hubei Sanli Fengxiang Technology Co., n.d.)

Apart from that, reducing the operating temperature is considered as other solution to enhance the reaction process since the reaction is already exothermic (Santaella et al., 2015).

However, decreasing the operating temperature is not recommended at all because it will diminish the reaction rate and induce to have bigger reactor volume for the process.

Therefore, slow mixing time and ineffective mass transfer between reactant, with low reaction rate of esterification are the significant problems that need to be solved. Chemical process that has better transport phenomena and have higher reaction rate at lower residence time and optimum temperature with ideal usage of reactant are the fundamental goals to produce high revenue of ethyl ethanoate for food industry.

Process-intensifying equipment has the potential to solve these problems because it offers effective mass transfer between the reactants and energy-efficient even at smaller number or size of process equipment (Stankiewicz and Moulijn, 2000). It also can improve the sustainability in the chemical industry. A novel intensified process equipment called coiled flow inverter (CFI) is found to have excellent mixing efficiency and produce higher reaction rate in a shorter time (Parida et al., 2014, Mandal et al., 2011a, Mandal et al., 2011b). Hence, in this study, a novel intensified process equipment called coiled flow inverter (CFI) is utilized to perform esterification reaction involving ethanol and acetic acid in solvent-free and catalyst-free condition for safety purposes. Detailed explanation on the implementation of the study and its results were presented in this paper.

## **1.2 Objectives**

1. To investigate the mixing performance of coiled flow inverter when applying very slow and high laminar Reynold Number of reactants
2. To elucidate the effect of synthesis parameters in achieving higher yield at shorter time
3. To study the optimum parameters of ethyl ethanoate synthesis in CFI using CFD tool

### 1.3 Scope of Study

In this study, esterification reaction between ethanol and acetic acid in CFI under solvent-free and catalyst-free conditions was studied. The acetic acid and ethanol were used as the reactants for esterification process to produce ethyl ethanoate or known as ethyl acetate as the main product and water as the by-products. This esterification synthesis was investigated under two conditions, very low laminar Re ( $Re < 1$ ) and high laminar Re ( $Re > 25$ ). To determine the acid conversion and ethyl ethanoate yield, titration analysis was used instead of the more accurate gas chromatography analysis due to the limited number of gas chromatography available in the university and the breakdown of gas chromatography in the analytic laboratory. Moreover, conducting the analysis via gas chromatography is time consuming and at the same time, limited time available to do the analysis. Therefore, the experimental results analysis was done via titration method. After obtaining the results from the experiments, the values of forward rate constant for those two laminar conditions were determined and simulated in COMSOL with a predefined CFI geometry design for the experiment. Then, the kinetics reaction of the experiment sets that resulted the highest conversion and ethyl acetate concentration under very low and high laminar Re were chosen as the inputs for simulation involving different CFI parameters, either internal diameter of tube or coil diameter. Comparison of simulation results for different CFI parameters were observed and discussed to identify the optimum parameters that promotes acid conversion and ethyl acetate production.

## **CHAPTER 2 LITERATURE REVIEW**

### **2.1 Overview**

In previous chapter, utilizing acid catalyst in Fischer esterification process of ethanol and acetic acid method is not encourageable because it may affect the quality of food. Hence, further discussion regarding applicability of the catalyst and solvent in food are recommended to determine the best way to produce ethyl ethanoate. Besides that, the potential solutions to replace conventional equipment along with having intensified mixing and mass transfer between the reactants at optimum conditions will be explained in this Chapter 2. This chapter will present literature reviews related to common esterification process of ethanol and acetic acid, conventional equipment used for synthesis ethyl ethanoate, application of process-intensifying equipment for reaction process especially esterification reaction, CFI geometries that has been studied in other computational fluid dynamics (CFD) software and their mesh analysis.

### **2.2 Esterification process of ethanol and acetic acid**

In industries, ethyl acetate or ethyl ethanoate is commonly synthesized by esterification of ethanol and acetic acid due to its simplicity in processing (Guo et al., 2014). Catalysts are used in esterification to increase the production rate and volume towards highly efficient reaction. Moreover, the protonation of carboxylic acid, in this case, acetic acid requires catalyst for the reaction mechanism to proceed (Zeki et al., 2010). Thus, it is crucial to choose the best catalyst for the process. Based on the previous studies, esterification of ethanol and acetic acid has been done either with homogenous or heterogenous catalyst.

Zeki et al. (2010) had conducted several experiments on investigating the effects of adding excess ethanol and increasing temperature towards the esterification process of acetic acid and ethanol catalyzed by homogenous catalyst, which is sulphuric acid. The experiment

achieved 80% conversion of reactants to ethyl ethanoate and water at 60°C with molar ratio of 10 : 1 ethanol to acetic acid. Based on the experiment, higher temperature and lower molar ratio of ethanol and acetic acid were identified as the main contributors towards the increment of reactant conversion. In fact, the presence of homogenous catalysts such as hydrochloric acid, sulphuric acid and strong organic acids also helps to increase conversion since they are very effective and strong acid catalysts.

Homogenous catalyst presents in the same phase as the reactant phase which helps to provide higher catalytic efficiency since more contact may happen between catalyst molecules and reactants that are in the same phase (Guo et al., 2014). However, it is difficult to separate them from final products which coexist in liquid form as well and lead to waste of catalyst since it is non-recyclable catalyst. Moreover, it may cause equipment corrosion and dehydration of alcohol if excess catalyst is added (Blanchard and Brennecke, 2001). Utilizing heterogenous catalysts such as solid acids and ion exchange resins provides better solution to the issues mentioned earlier. This catalyst is considered as one of the catalysts which performs better in separating reactant from product, provides higher catalyst recovery and more applicable in continuous esterification (Guo et al., 2014).

De Silva et al. (2014) had investigated the effectiveness of using low-cost ion exchange resin, Trilite SCR-B as heterogenous catalyst in esterification of ethanol and acetic acid. Heterogenous kinetic models Langmuir-Hinshelwood (LH) is applied as it correlated better with the previous experimental results and the reaction was conducted within temperature range of 61°C to 81 °C with molar ratio of ethanol to acetic acid 1:1 and catalyst loading of 50g/L. They discovered that ion exchange resin makes the reaction faster. Reaction at 81 °C reached about 54% conversion which is the highest that can be achieved in 40 minutes compared to other reaction at 61°C and 72°C. The highest conversion that can be achieved when using Trilite SCR-B throughout the reaction at 81 °C is only around 56% to 58%.

Hasanoğlu et al. (2009) also had executed several esterification experiments in a pervaporation membrane reactor using homogenous and heterogenous catalysts separately. They used sulphuric acid as homogenous catalyst and Amberlyst-15 as heterogenous catalyst for esterification process of ethanol and acetic acid. Pervaporation membrane reactor was equipped with polydimethylsiloxane (PDMS) as the membrane material to improve the conversions through the removal of one or more products generated during the reactions. Both experiments were done with and without the membrane within temperature range of 50°C to 70°C with molar ratio of ethanol to acetic 1 : 1 and 3 : 2. In the experiment involving Amberlyst-15, the batch pervaporation membrane reactor is found to have greater conversion compared to the batch reactor without membrane. The highest conversion that can be achieved among these experiments is about 78% at 70°C with 1.5 molar ratio for ethanol to acetic acid, operated in reactor equipped with pervaporation membrane. Nevertheless, reaction at temperature of 60°C only able to reach 70% conversion as heterogenous catalyst is added into the reaction. As for the experiments with sulphuric acid at 60°C, the conversion of the reactant was higher than the conversion acquired with Amberlyst-15 at similar operating condition. This proves that homogenous catalyst is more effective in increasing the esterification rate and reactants conversion compared to heterogenous catalyst. Sadly, these catalysts are not suitable to be applied in production centres anymore due to its corrosiveness, instability and high cost (He et al., 2014, Zhao et al., 2006). Some of the homogeneous catalysts are not eco-friendly and cause complexity in disposal process.

Therefore, Blanchard and Brennecke (2001) and He et al. (2014) conducted a study on the effects of using ionic liquids (ILs) as the substitute for hazardous liquid acids solvent in esterification process. . Ionic liquids (ILs) have been certified as a green solvent due to their low vapour pressure, good solvent properties, outstanding thermal stability, and their capability in expediting their recyclability at the end of the esterification process. Mostly, acidic ILs are

used as catalyst and reaction medium like 1-butylpyridinium chloride-aluminium (III) chloride, hydrogen sulphate and sulphonic acid-functionalized ILs. In He et al. (2014) work, they synthesized five halogen-free amphiphilic Brønsted acidic ionic liquids based on 3-(*N,N*-dimethylalkylammonium)-propanesulphonate quaternary ammonium zwitterions and *p*-toluene sulphonic acid monohydrate and exploited them as dual-solvent catalyst for several esterification of different carboxylic acids and alcohols under normal condition. They found out that the reactant conversions achieved 82.2% which shows a satisfying result, when 3-(*N,N*-dimethylstearylammmonium) propanesulphonic acid *p*-toluenesulphonate ([DSPA][Tos]) was added as solvent at reaction temperature of 60°C

Alternatively, high-pressurized supercritical carbon dioxide technology presents a good solvent replacement for hazardous organic liquids to produce esters (Blanchard and Brennecke, 2001). The environmentally benign compound, carbon dioxide may alter the fugacity coefficients of each substances involved in the reaction and drive towards higher reaction rate. Transferring the product into other phase would likely ascend the conversion percentage for instance, forming aqueous-rich liquid phase. The uncatalyzed esterification reaction was conducted at 60°C and 58.6 bar of carbon dioxide where liquid phase and dense gas phase were formed. At this operating condition, the yield or extent of reaction might deviate a bit. This reaction can occur even without catalyst and able to increase the conversion to 72% high-pressure carbon dioxide solvent. It would be safer to use supercritical carbon dioxide as the solvent for synthesizing ethyl ethanoate instead of resorting only towards the reaction with catalyst.

Nonetheless, it is very expensive to have high pressure equipment in order to create high-pressure carbon dioxide as the medium in this esterification reaction. It is also dangerous to perform a process at high pressure. Even though, it is non-toxic, facilitate in separating it from the product, non-flammable and environmental-friendly solvent, it has its own drawbacks



that will make the thermodynamics system of the reaction become more complex. It cannot be applied to dissolve polar molecules as it is non-polar extraction fluid (Abbas et al., 2008). Thus, it is the safer not to add any catalyst or solvent in the esterification reaction to form ethyl acetate as food derivative.

Bankole (2011) has done a research on uncatalyzed and solvent-free esterification of ethanol and acetic acid in capillary batch reactor. The reaction was carried out at high temperature ranging from 100 °C to 250 °C with equimolar amount of ethanol and reported that the conversion of the reactant increases along with increasing temperature. At 250 °C, the reaction able to reach about 65% conversion in 60 minutes. Calvar et al. (2007) also found out in their work that uncatalyzed esterification has higher conversion percentage compared to reaction catalyzed using acid resins. This happens because acid resins tend to selectively adsorb reactants. This uncatalyzed esterification is not quite popular in industry since it requires longer processing time and need to operate at higher temperature to obtain high conversion. Improving the equipment used or using advanced technology might be the solution for uncatalyzed esterification to enhance their performance in producing ethyl ethanoate in shorter time.

## **2.3 Unit Operation Equipment Used for Esterification Process**

### **2.3.1 Esterification Process in Conventional Equipment**

Initially, esterification reaction to yield ethyl ethanoate is carried out in a batch stirred reactor. Agitator is required to mix acetic acid, ethanol and supplementary catalyst or solvent to enhance the mass transfer between the reactants and speed up the reaction time. The greater the mass transfer rate and surface contact between the reactants, the higher the production efficiency. Hence, stirrer is important to double up the reaction mixing. Obi and Okoye (2016) conducted a kinetic study and synthesis of ethyl ethanoate using eco-friendly solid catalyst, which is clay catalyst in a stirred reactor. The reaction was executed in batch mode at 90°C

with different molar ratio of reactants. They discovered that maximum conversion of acetic acid to produce ethyl ethanoate can be acquired at 90°C after 150 minutes with molar ratio of acetic acid and ethanol 2 : 1 and 2 grams of catalyst.

Apart from that, İnce (2002) conducted esterification experiment with diluted acetic acid and ethanol with assistance of acidic polymer catalyst in batch reactor too. The catalyst used is the synthetic acidic resin Lewatit (Bayer AG) and the maximum conversion that can be attained is about 55% with 1 : 1 molar ratio of ethanol to acetic acid and 20% of catalyst loading at 80 °C reaction temperature. Besides that, both Beula and Sai (2015) and KIRBAŞLAR et al. (2001) also exploited esterification reaction of ethyl ethanoate in isothermal batch reactor with the assistance of catalysts at temperature ranging from 50 °C to 80 °C.

Mandake et al. (2013) had fully utilized a glass reactor with 7.5 cm internal diameter with four equivalent baffles and four-bladed turbine impeller for synthesizing methyl acetate from acetic acid and methanol mixture. The experiment was carried out with and without any catalyst or solvent to examine the effects of catalyst presents in esterification process of methanol and acetic acid. At the same molar ratios, the non-catalytic reaction achieved 14.5 % conversion while the catalysed reaction increases to 54 % after 3 hours.

In 2011, Bankole (2011) has carried out few experiments regarding esterification involving biomass-derived carboxylic acids in capillary batch reactors filled with corrosion-resistant quartz tubes. The tubes with dimensions of 2 mm internal diameter and 6 mm outer diameter were used to avoid any compound vaporization from the reaction medium. The experiment of esterification reaction containing acetic acid and ethanol was conducted at temperature 100 °C, 150 °C, 200 °C and 250 °C. Based on their results, the highest conversion that can be achieved at highest temperature (250 °C) is 65% in 60 minutes while the lowest conversion is 30% at 100 °C in 360 minutes. These processes use very high temperature but obtained conversion lower than 80%.

Majority of the researches conducted utilized catalyst to aid their acetic acid esterification process in reactor. Standard reactor has bigger volume and stirrer to avoid stagnant flow during the mixing. However, it will require longer reaction time and cause inefficient mixing which lead to lower conversion of reactants. Hot spots also might be the root cause of low reactant conversion. Due to unsatisfactory conversion achieved from the experiment, the researchers exploited esterification reaction in distillation column to get high purity of ethyl ethanoate. Apparently, synthesizing acetates may arise some issues, for instance equilibrium limitation which exists from reversible reaction of alcohols and acetic acid (Lai et al., 2007). Hence, the audacity to apply distillation column has increased among the ethyl acetate manufacturers. However, adding equipment will increase the capital and maintenance cost. Therefore, more competitive and vast research of studies are done on intensified equipment like reactive distillation column that can undergo reaction and distillation simultaneously in a single unit (Elgue et al., 2002). It is not only able to enhance the equilibrium limited reaction conversion, it also can save the operational and capital costs since no additional equipment is needed to separate and purify the product after undergoes process reaction (Lai et al., 2007, Elgue et al., 2002).

### **2.3.2 Implementing Esterification Reaction in Process-Intensifying Equipment**

#### **2.3.2(a) Reactive Distillation Column**

Tang et al. (2003) applied reactive distillation system in manufacturing ethyl ethanoate from mixture of acetic acid, ethanol and sulphuric acid homogeneous catalyst. They obtained 99.5% of ethyl ethanoate composition at the top product and designed two reactive distillation for that purposes. Besides that, Santaella et al. (2015) also utilized reactive distillation column for ethyl ethanoate synthesis. They carried out the reaction process with the assistance of different types of catalysts such as hydrochloric acid, sulphuric acid, Amberlyst-15, Amberlyst-35, Amberlyst-36, Amberlyst-70, Purolite CT179 and auto-catalytic reaction in the reactive

distillation separately to study those catalysts effects towards reactant conversion catalysts. In their investigation, Amberlyst-15, sulphuric acid catalyst and auto catalyst had utilized two different rate of reaction and parameters which resulted different values of conversion. It was reported that both auto-catalytic reactions have reactant conversion above than 20 % at higher residence time when operated at 80 °C and 1 : 1 molar ratio of ethanol and acetic acid. This proves the need of adding catalyst into the reaction to achieve higher conversion of ethyl ethanoate. Thus, based on their research, Amberlyst-15-1 resulted the highest conversion (around 68%) in shortest time.

Meanwhile, a pilot-scale ethyl ethanoate plant had been studied by Lai et al. (2007) to produce high-purity ethyl ethanoate in reactive distillation (RD). The plant was designated to have one reactive distillation with a decanter and a downstream stripper. In their work, they used 95.5 wt% of ethyl alcohol, 99 wt% of industrial grade acetic acid with water as impurity and operated below azeotropic condition into RD to improve the reactant conversion. Amberlyst-35 wet was added as acidic ion-exchange resin to catalyse the process. In the end of experiments, they successfully obtained up to 99.5 wt% high purity of ethyl ethanoate or well-known as ethyl acetate with developed efficient start-up procedure.

The reactive distillation not only can handle catalysed reaction, but also valid for uncatalyzed reaction. Non-catalytic esterification of acetic acid and ethanol in a reactive distillation had been implemented by Bock et al. (1997) due to the reactive system and specialties of this advanced intensified equipment. All of the difficulties that emerge in acetic acid esterification before were inspected through rigorous model. The esterification conversion in their case was affected by the distillation properties such as number of reactive stages and holdup. Basically, uncatalyzed reaction will tend to have longer reaction time but the conversion will increase with higher residence time due to bigger holdup was set in reactive distillation column.

Other than reactive distillation, there is a study on the influence of pulsed electric fields (PEF) towards the esterification reaction between acetic acid and ethanol without any catalyst. Lin et al. (2012) aimed to explore more ecological reaction procedure which does not depend on the reactants concentration, catalyst and high temperature to promote esterification productivity in food industry. They applied process-intensifying method which uses alternative forms of energy like electric fields to accelerate the liquid-liquid process reaction. Better adhesion properties can be obtained when the reactants' droplets are electrically charged by electric field (Stankiewicz and Moulijn, 2000). It was disclosed that PEF able to enhance the esterification reaction at lower temperature. This happened because lower temperature caused the atoms that were available at lower electron energy conversion became more excited after they were exposed to the pulsed electric field. Eventually, they were easily transported to a higher activity level. Therefore, PEF conditions are suitable for esterification process since it fits well with the requirement of food processing that prefer the food processing to be done at lower temperature (Lin et al., 2012).

### **2.3.2(b) Micro-Structured Reactor**

Besides that, micro-structured reactor, another type of process-intensifying equipment has become more popular for esterification reaction nowadays. Microreactors are chemical reactors built in smaller dimensions, have multiple layers and micro-sized channels. It is widely used in organic synthesis, mixing, catalytic reaction, heat exchange and separation as it is able to integrate all these functions in a single unit (Stankiewicz and Moulijn, 2000). It provides excellent mass transfer rates because of greater interfacial forces exists and form complex flow patterns (López-Guajardo et al., 2017). Thus, the process yields more products within short residence time and allows highly exothermic processes to operate in it isothermally.

Due to special features of microreactor, Kulkarni et al. (2008) had conducted synthesis of butyl acetate from n-butanol and acetic acid in interdigital micromixer, catalysed by

sulphuric acid and Amberlyst-15. It was performed at temperature 80 °C with different feed flow rate. The esterification process became faster in microreactor and able to achieve 85% of acetic acid conversion when the feed flow rate was 0.1 mL/min and feed ratio of n-butanol to acetic acid was 30 : 70.

Since food industry prefer to process food without catalyst and solvent, El Zanati et al. (2017) moved one step further by integrating ethanol and 2-ethyl hexanoic acid for esterification process in designated Y-shaped microreactor. This new design microreactor had two inlet and one outlet microchannels. Another multi-microchannels microreactor also was designed by them to increase the efficiency of microreactor. The reaction was undergone at 1 : 1 molar ratio of ethanol to 2-ethylhexanoic acid at 25 °C to 65 °C. The result analysis showed that the end-product of reaction was purely ester with purity of 95.81% maximum and about 99.6 % conversion was achieved at 65 °C. It was recorded that the high purity of product was successfully collected because of fast reaction in the channel of Y-shaped single channel microreactor. No reaction reversibility may occur during the process as low residence time in channel as well. As for reaction in multi-channel microreactor where the operating conditions was 1 : 1 molar ratio of ethanol to 2-ethylhexanoic acid with feed flow rate at 4 cm<sup>3</sup>/min and 25 °C, the reaction conversion almost reached 100% in 80 seconds. This demonstrated multi-channel microreactor really enhance the reaction conversion to the maximum level rather than Y-shaped single channel microreactor.

Yao et al. (2009) had started using microchannel reactor earlier in their research work on the synthesis of acetic acid esters with *p*-toluene sulphonic acid (PTSA) as homogenous catalyst. The microchannel reactor with internal diameter of 0.25 mm was exploited for esterification of acetic acid with different alcohols. The ethyl ethanoate synthesis reaction able to reach 80 % conversion at 85 °C with 6 % catalyst dosage. The higher the catalyst quantity, the higher the reactant conversion. The yield of acetic acid esters also accelerated rapidly as

the residence time increased in the microreactor. The most suitable residence time in this work was 14.7 minutes as high yield of ethyl acetate or ethyl ethanoate can be obtained within this time (70.1 %).

Recently, further research is continuously done on upgrading microreactor or inventing new technologies to double up the conversion and the reaction efficiency. In industry, helically coiled tubes are introduced on the microreactor since it can operate as residence time reactor, heat exchanger and even static mixer. (Gürsel et al., 2016, Kumar et al., 2006, Kurt et al., 2015). The helically coiled tubes boost up fluid mixing by allowing centrifugal force applied on the flow inside the tube and develop into Dean Flow which will create symmetrical vortices on the tube cross section. This secondary flow helps to promote radial mixing at laminar flow regimes and eliminates axial dispersion in tubes. In this way, it generates the narrowest residence time distribution (RTD) along the tubes.

A coiled tubular reactor with dimensions 3.2 mm outer diameter, 1.2 mm internal diameter and 84 m length was handled by Phaiboonsilpa et al. (2020) to regulate the reaction between ethanol and acetic acid producing ethyl ethanoate or ethyl acetate in supercritical ethanol. This catalyst-free esterification reaction was found to give the best outcomes at 270 °C, 20 MPa, and 1 : 1 molar ratio of acetic acid to ethanol. It resulted the maximum yield of ethyl ethanoate (89 mol%) in 60 minutes. This proves coiled microreactor really able to intensify the fluid mixing of reaction.

More enhancements towards the reactive phases mixing can be acquired by inducing chaotic advection via flow disruption. Saxena and Nigam (1984) had conducted a study on the aftermath of introducing disruption towards the reaction flow in helical coiled tubes. They designed equally size of 90° bends along the tube to create flow inversions. This design unexpectedly narrowing the flow and reduce the residence time distribution (RTD) in the tubes.

As the result, the helical coiled tubes behaved as plug flow reactor. They successfully invented this new miniaturization equipment and named it as coiled flow inverter (CFI).

### **2.3.2(c) Coiled Flow Inverter (CFI)**

This coiled flow inverter is declared as high-potential device for non-Newtonian fluids processing because of its specialties in enhancing fluid mixing and heat transfer (Singh et al., 2013). It can be applied as heat exchanger, membrane, microreactor for metal extraction or motionless mixer for gas-liquid-liquid reactions, mass transfer purposes, food processing, and pharmaceuticals. Its novel design has square-duct structure armed with helically coiled tubes around its edges (Soni et al., 2019). In this equipment, the flow will change direction continuously as well as the vortex formation plane due to the changes of centrifugal force direction created by the helical coil bends. This 90° bend indeed enhances the mixing of fluids and provides constant temperature condition along CFI (Singh et al., 2013).

Mandal et al. (2011b) had done numerical simulation to study the performance of free-radical styrene polymerization in CFI. They found out that CFI had better performance at lower diffusion coefficients of fluid. It also provided excellent efficiency even with few bends. The heat transfer in CFI was greatly reduced within four bends of CFI since the flow inversion generated accommodate the fluid temperature inside CFI (Kumar et al., 2007). This strongly validate its important in food processing as it certainly gives higher heat transfer ad mixing efficiency.

Atom transfer radical polymerization (ATRP) to synthesize linear and branched 2-(dimethylamino)ethyl methacrylate (PDMAEMA) was also conducted in CFI to narrow down the residence time distributions (RTD) and gain enhanced mixing throughout the polymerization process (Parida et al., 2014). In addition, it was reported that ATRP reaction can be speed up by operating them in microreactor (Parida et al., 2012) and have excellent branching structures rather than batch reactors (Bally et al., 2011). As the results, CFI was



found to have the highest branching efficiency, followed by coiled tubes and lastly, batch reactor. This great efficiency in branching influenced the unification of branching points in polymer chain to become more dominating. CFI also had successfully boosted fluid mixing and it contributed towards diminishing polydispersity index (PDI) of synthesized linear PDMAEMA.

Although few studies have been conducted on the liquid-liquid extraction and liquid-liquid reactive system especially for polymerization and transesterification, this novel device has not been broadly explored for esterification reaction and has not undergoes any engineering simulation. Moreover, only few studies were found for uncatalyzed and solvent-free esterification reaction of acetic acid and ethanol in other equipment, but the results of the reaction were not as desired and very unsatisfactory due to longer time of reaction and low conversion of the reactants. Hence, in this present work, computational fluid dynamics (CFD) study will be conducted via COMSOL Multiphysics 5.5 to simulate non-catalytic and solvent-free esterification of acetic acid and ethanol in CFI and observe the flow mixing patterns and its effectiveness under varying parameters.

## **2.4 CFI Geometry**

During the first invention of CFI, few geometry parameters of CFI was discussed by Saxena and Nigam (1984). Bend location, angle of bend on RTD, number of bends, dean number on RTD of bend coils, presence of coils, spacing between bends are crucial in designing CFI and need to be optimized in order to have the best outcomes from CFI. It was the best to place the coils at the midway of flow duct too. It was observed that the higher the number of bends, the smaller the residence time distribution. Besides, straight coiled tubes were not as efficient as bent coiled tubes due to high residence time inside it.

The researchers also learnt that higher number of bends in CFI will narrow down the RTD curve. It will also produce greater radial mixing because of the direction of inversion of velocity profile is the same as the bending. Besides that, number of turns will decide the tube length needed for one coil. It will affect the improvements of Dean vortices in helically coiled tubes. In fact, pitch distance also will influence Dean vortices developments as it is related to the torsion effects. The further the pitch distance, the faster the Dean vortices disappear, and the velocity profile of CFI will become equal as the velocity of laminar flow in straight pipe. Not only that, coil, inner tube, and coil tube diameter also need to be chosen properly as it is closely related to formation of Dean vortices and flow profile. Last but not least, 90° bending angle with equal single coil length before and after the bends are recommended as it will give the narrowest RTD for CFI (Kurt et al., 2015). With all these general research and information, these CFI geometries can be disserted in future work. Improved bent coiled geometry will lead to better formation of secondary flow in the equipment (Jha et al., 2020).

In 2014, a comparison study between different geometry of microreactor had been made which involved coiled tube and coiled flow inverter microreactors. (Parida et al., 2014) used same 3 m length, 876  $\mu\text{m}$  internal diameter and number of coils for both microreactors. However, all stainless-steel coiled tube reactor was in straight position while coiled flow inverter reactor had 90 °C bends at identical interval of CFI as in Figure 2.1. Square-duct geometry of CFI was formed with three bends and equal number of coils at each bends. These two different geometries were used for linear and branched atom transfer radical polymerization (ATRP) process. At the end of the experiments, CFI was reported to have great performance since it can control the polymer characteristics with even better flow mixing behaviour and effectiveness of branching rather than microreactor with straight coiled tube geometry.

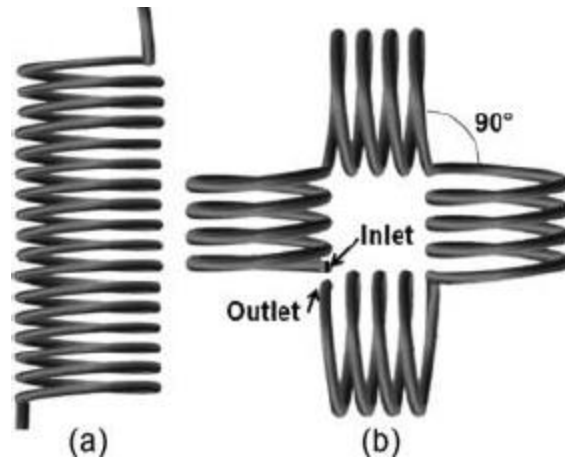


Figure 2.1 (a) Straight coiled tube microreactor (b) Coil flow inverter microreactor (Parida et al., 2014)

Jha et al. (2020) compared different geometries of CFI in their research. They innovated standard coiled flow inverter (CFI) design into asymmetrical compact coiled flow inverter (ACCFI) and symmetrical compact coiled flow inverter (SCCFI). All of them had similar inner tube diameter (0.003 m), coil diameter (0.031 m), coil pitch (0.006 m) and 10.33 curvature ratio. Both standard CFI and symmetrical CCFI had equal length of coil which is 6.12 m while asymmetrical CCFI was 6.54 m long. The difference between them is the number of bends. CFI had three 90 °C bends and 16 turns on each equal arm length while ACCFI had 6 bends and four turns on each variable arm lengths. SCCFI was designed to have 15 equidistant 90 °C bends and four turns on each equal coiled tube arm length. From the results obtained, it was discovered that SCCFI had the maximum narrowing of RTD since the unique RTD for SCCFI was at the highest Dean number. Unique RTD defines the maximum radial mixing achieved and how impregnated RTD narrowing is in a design. Higher Dean number exhibits strong radial mixing in the device because of stronger centrifugal forces acted on the fluid. This will cause RTD becomes almost likely as the ideal plug flow condition. Hence, having unique RTD at higher Dean number creates almost ideal plug flow condition due to narrower RTD generated. Besides that, since SCCFI had the highest number of bends, it had the highest mixing

characteristics compared to the other CFIs. In overall of the study, SCCFI possesses the most suitable geometry for excellent performance in any operations.

Another CFI geometry was found and used by Gürsel et al. (2016). They created CFI with 3.2 mm internal diameter and 6.35 mm outer diameter coiled tubes attached to 25.4 mm outer diameter stainless steel cylindrical bar that formed square-structure shape. It was used for liquid-liquid extraction experiment with phase separator. The curvature ratio used for this CFI was 10 and have coil diameter of 32 mm. It had three 90° bends and 4 tube turns at each side of equal tube lengths. They detected CFI had increased extraction efficiency higher than process in straight tube even at lower flow rates. Furthermore, it was able to maintain the excellent extraction performance because of chaotic advection formed from Dean vortices and flow inversions. Again, this shows that CFI is an advanced device with great, unbeatable performance. Other CFI geometries available in other articles are summarized in Table 2-1.

Table 2-1 CFI geometries used in other literature

Process	CFI Geometry					References
	Internal Diameter, mm	Number of Turns at Each Sides	Angle of bends	Number of bends	Curvature ratio, $\lambda$	
<b>Polymerization</b>	0.876	4 turns of equal tube length	90°	3	-	(Parida et al., 2014)
<b>Mixing of miscible fluids</b>	0.5	4 turns of equal tube lengths	90°	3	10	(Soh and Supriyanto, 2017)
<b>pH Level Distribution</b>	3.2	5 turns of equal tube lengths	90°	39	21.7	(David et al., 2020)