LITERATURE REVIEW

1. Biodiesel

Biodiesel, an alternative energy, is usually made by a chemical reaction of alcohol and vegetable, animal or waste cooking oils. Biodiesel can be used as a pure fuel or blended with petroleum. Much of the world uses a system known as the "B" factor to state the amount of biodiesel in any fuel mix. The mixing of 20 percent by volume biodiesel with 80 percent by volume petroleum diesel is called B20 and pure biodiesel is referred to as B100. Using biodiesel in a conventional diesel engine reduced unburned hydrocarbons, carbon monoxide, and particulate matter compared to emissions from diesel fuel. This is because burning ancient fossil fuel adds carbon to the atmosphere upsetting the carbon balance, while growing part of our fuel consumes carbon in the growing process and then releases it in combustion.

There are variety of oils can be used to produced biodiesel such as vegetable oil, waste cooking oil and animal fat. Focusing on the vegetable oil, rapeseed and soybean are most commonly used and others are corn, peanut, rapeseed, soybean, sunflower and jatropha. Basically, all vegetable oils and animal fats consist of triglyceride (TG) molecules as shown in Figure 1.

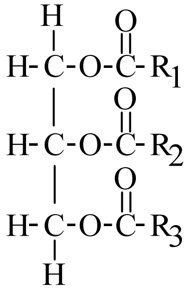


Figure 1 Triglyceride

R1, R2 and R3 represent the hydrocarbon chain of the fatty acyl groups of the triglyceride. The properties of biodiesel depend on the amount of fatty acid. Fatty acid is designated by two numbers. First is the total number of carbon atom in the fatty acid chain and second is the number of double bounds in the chain. For example, 16:0 has a 16 atom of carbon and zero double bounds in molecule. The fatty acid of vegetable oils is summarized in the Table 1. Natural vegetable oils and animal fats are extracted or pressed to obtain crude oil or fat. These usually contain free fatty acids, phospholipids, sterols, water and other impurities. The free fatty acid and water contents have the significant effect on transesterification reaction of triglycerides with alcohols using alkaline or acid catalysts.

Table 1 Chemical properties of vegetable oil

Vegetable Oil	Fatty acid composition, % by weight								
	16:0	18:0	20:0	22:0	24:0	18:1	22:1	18:2	18:3
Corn	11.67	1.85	0.24	0.00	0.00	25.16	0.00	60.6	0.48
Cottonseed	28.33	0.89	0.00	0.00	0.00	13.27	0.00	57.51	0.00
Crambe	2.07	0.7	2.09	0.8	1.12	18.86	58.51	9	6.85
Peanut	11.38	2.39	1.32	2.52	1.23	48.28	0.00	31.95	0.93
Rapeseed	3.49	0.85	0.00	0.00	0.00	64.4	0.00	22.3	8.23
Soybean	11.75	3.15	0.00	0.00	0.00	23.26	0.00	55.53	6.31
Sunflower	6.08	3.26	0.00	0.00	0.00	16.93	0.00	73.73	0.00
Poppyseed	12.6	4	0.00	0.00	0.00	22.3	0.00	60.2	0.5
Safflower	7.3	1.9	0.00	0.00	0.00	13.6	0.00	77.2	0.00
Seameseed	13.1	3.9	0.00	0.00	0.00	52.8	0.00	30.2	0.00
Linseed	5.1	2.5	0.00	0.00	0.00	18.9	0.00	18.1	55.1
Wheat grain	20.6	1.1	0.00	0.00	0.00	16.6	0.00	56	2.9
Palm	42.6	4.4	0.00	0.00	0.00	40.5	0.00	10.1	0.2
Tallow	23.3	19.3	0.00	0.00	0.00	42.4	0.00	2.9	0.9
Hazeelnot kernel	4.9	2.6	0.00	0.00	0.00	83.6	0.00	8.5	0.2
Walnut kernel	7.2	1.9	0.00	0.00	0.00	18.5	0.00	56	16.2
Almond kernel	6.5	1.4	0.00	0.00	0.00	70.7	0.00	20	0.00
Olive kernel	5	1.6	0.00	0.00	0.00	74.7	0.00	17.6	0.00

[a] Wheat grain oil contains 11.4% of 8:0 and 0.4% of 14:0 fatty acids.

Source: Demirbas. (2002)

The using direct vegetable oil or blending with the oil is not satisfied. The high viscosity, acid composition, free fatty acid content, gum formation due to oxidation and polymerization during storage and combustion, carbon deposits and lubricating may cause some problem (Harwood, 1984). To solve this problem, there are many techniques for converting the vegetable oil to biodiesel such as transesterification, pyrolysis, enzyme lipase, super critical fluid extraction.

In addition, there are common international standard for biodiesel (i.e. EN 14214, ASTM D 6751). The standards of the fuel production should be: (1) complete reaction (2) removal of glycerin (3) removal of catalyst (4) removal alcohol (5) absence of free fatty acid (6) low sulfur content. Table 2 shows the biodiesel specification of EN 14214 and ASTM D 6751.

Table 2 The biodiesel specification between EN 14214 and ASTM D 6751.

Properties	EN 14214		ASTM D 6751	
	Unit	Limits	Unit	Limits
Ester content	% (m/m)	96.5	-	-
Density at 15 °C	kg/m^3	860-900	-	-
Viscosity at 40 °C	mm^2/s	3.5-5.0	mm^2/sec	1.9-6.0
Flash point	°C	120 min	°C	130 min
Sulfur content	mg/kg	10 max	% mass	0.05 max
Carbon residue	% (m/m)	0.3 max	% mass	0.05 max
Cetane number		51 min		47 min
Sulfated ash	% (m/m)	0.02 max	% mass	0.02 max
Water content	mg/kg	500 max	% volume	0.05 max
Total contamination	mg/kg	24 max	-	-
Copper strip corrosion	rating	class 1		No. 3 max
Cloud point	-	-	°C	Report
Oxidation stability	hours	6 min	-	-
Acid value	mg KOH/g	0.5 max	mg KOH/g	0.8 max
Iodine value	g/100g	120 max	-	-
Linoolenic acid ME	% (m/m)	12 max	-	-
Polyunsat ME	% (m/m)	1 max	-	-

Table 2 The biodiesel specification between EN 14214 and ASTM D 6751. (cont'd)

Properties	EN 14214		ASTM D 6751	
	Unit	Limits	Unit	Limits
Methanol content	% (m/m)	0.2 max	-	-
Monoglyceride	% (m/m)	0.8 max	-	-
Diglyceride	% (m/m)	0.2 max	-	-
Triglyceride	% (m/m)	0.2 max	-	-
Free glycerol	% (m/m)	0.02 max	% (m/m)	0.02
Total glycerol	% (m/m)	0.25 max	% (m/m)	0.24
Alkali metals (Na+K)	mg/kg	5 max	-	-
Phosphorus content	mg/kg	10 max	% mass	0.001 max
Distillation temp.	-	-	°C	360 max

2. Jatropha oil

Jatropha curcas L. is a multipurpose large shrub or small tree of Latin American origin. It is local adjusted throughout arid and semiarid tropical regions of the world with an average annual rainfall of between 300 and 1000. In Thailand, it is now found in many parts of the country. Jatropha grows on well-drained soils with good aeration and is well adapted to marginal soils with low nutrient content. It occurs mainly at lower altitudes (0-500 m) in areas with average annual temperatures well above 20° C but can grow at higher altitudes and tolerates slight frost. Its leaves and stems are toxic to animals, but after treatment, the seeds or seed cake can be used as an animal feed. Jatropha seeds contain about 35 % of non-edible oil. 6 kg of dry seeds gives about 1.2 liter of oil.

In Thailand, Jatropha oil becomes an alternative source for producing biodiesel instead of palm oil. There are many advantages such as price is not fluctuating, easy to establish, grow quickly and require minimum care. The composition of Jatropha oil is illustrated in the Table 3. The oleic and linoleic acid are the major composition.

Table 3 Fatty acid composition of Jatropha seed oil

Fatty acid	%
Palmitic acid (16:0)	14.66±0.17
Palmitoleic acid (16:1)	0.82±0.02
Stearic acid (18:0)	6.93±0.02
Oleic acid (18:1)	42.36±0.48
Linoleic acid (18:2)	35.21±0.56
Total saturated fatty acids	21.59%
Total unsaturated acids	78.39%

Sources: Chatakanonda *et al.* (2005)

3. Transesterification

The transesterification is the reaction between triglyceride and alcohol to form biodiesel and glycerol by using catalyst. The reaction is shown in the Figure 2.

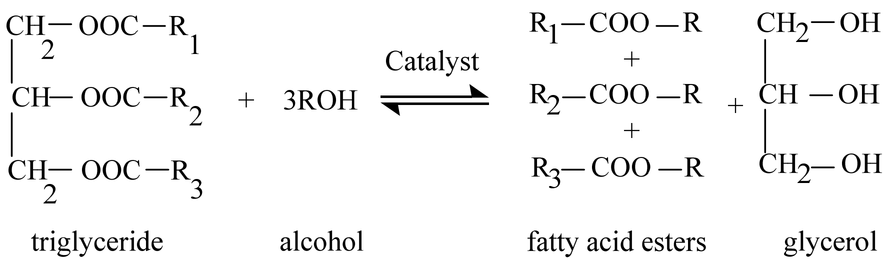


Figure 2 The transesterification reaction

The overall reaction consists of 3 stepwises with intermediate formation of diglycerides (DG) and monoglycerides (MG). The 3 step reactions are shown in the Figure 4. The alcohols that can be used in the tranesterification reaction are methanol, ethanol, propanol and butanol. Methanol is usually used because of low cost and its physical and chemical advantages (polar and shortest chain alcohol).The stecheometric between alcohol and the oil is 3:1. However, an excess of alcohol is usually more in order to shift the reaction to the right hand side.

$$\text{Triglyceride (TG)} + \text{ROH} \overset{\text{Catalyst}}{\rightleftharpoons} \text{Diglyceride (DG)} + \text{RCOOR}_1$$

$$\text{Diglyceride (DG)} + \text{ROH} \overset{\text{Catalyst}}{\rightleftharpoons} \text{Monoglyceride (MG)} + \text{RCOOR}_2$$

$$\text{Monoglyceride (MG)} + \text{ROH} \overset{\text{Catalyst}}{\rightleftharpoons} \text{Glycerol (GL)} + \text{RCOOR}_3$$

Figure 3 Three step of transesterification reaction.

The mechanism of alkali catalyst transesterification with vegetable oil (Schuchardt *et al.*, 1997) is shown in the Figure 4. There are consists of three steps. The first step is an attack on the carbonyl carbon atom by the methoxide ion ($CH3O^-$) to form a tetrahedral intermediate. In the second step, the tetrahedral intermediate reacts with an alcohol (methanol) to regenerate the anion of the alcohol. In the last step, rearrangement of the tetrahedral intermediate results in the formation of a fatty acid ester and a diglyceride. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol.

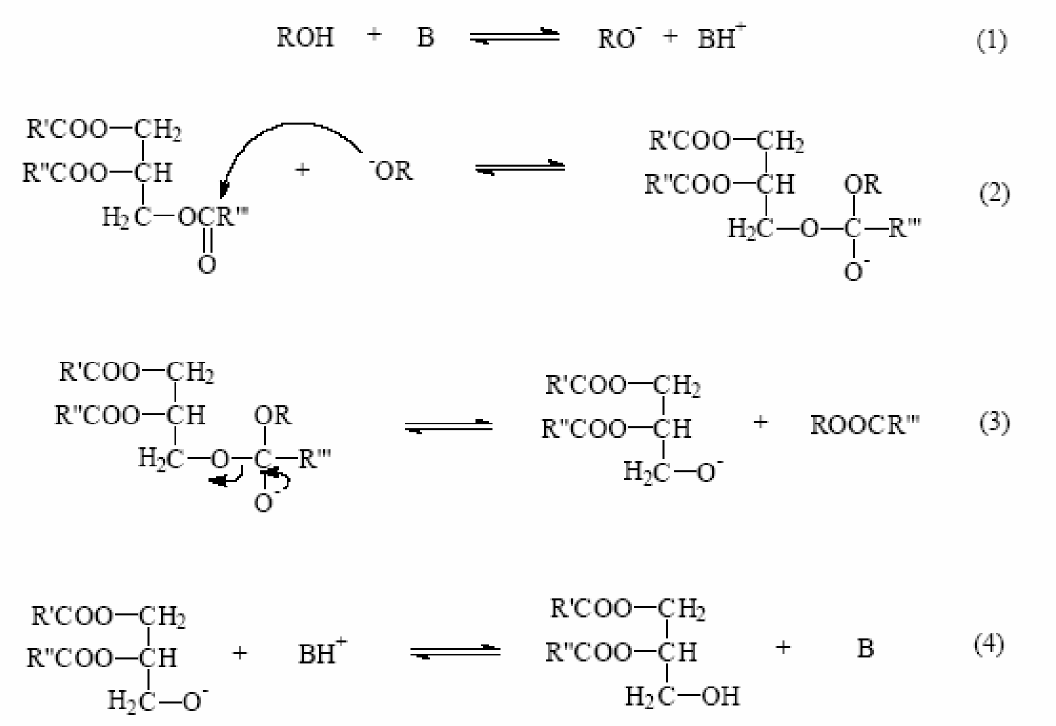


Figure 4 The mechanism of alkali catalyst transesterification

The transesterification reaction can be catalyzed by both homogeneous and heterogeneous catalyst. The advantages and disadvantages of each catalyst are described below.

Firstly, the common homogeneous are acid and alkali catalyst. Using alkali catalysts, the reaction is fast, high conversion and less corrosive than acid compound. However, hydroxide ion (OH^-) of alkali catalyst can react with the free fatty acid to produce soap. The soap formation is an undesirable side-reaction, because it partially consumes the catalyst, decreases the biodiesel yield and complicates the separation and purification steps (Vicent *et al.*, 2003). The removal of these catalysts is technically difficult and brings extra cost to the final product. In addition, the difficulty for recycling and the generation of large waste amounts make the traditional catalysts less favorable. The soap formation can be suppressed by using acid catalyst because there is no hydroxide ion. The acid reacts with free fatty acid to produce fatty acid esters, increasing the biodiesel yield. Nevertheless, the reaction of acid catalyst is lower than the acid and also needs more extreme temperature and pressure conditions.

Althought chemical transesterification using alkali catalyst process gives high conversion in small time. But it is difficult to removed glycerin and requires the waste water treatment. Therefore, using lipase as catalyst can overcome these problems. In addition, there are many advantages such as (1) possibility of regeneration and reuse (2) lower temperature of reaction (3) higher biodiesel. However, production cost of lipase catalyst is expensively than alkaline one.

Furthermore, other technique to produce biodiesel is transesterification using supercritical fluids. Saka and Kusdiana (2001) studied biodiesel production in super critical methanol. They demonstrated that preheating to 350 °C and treatment for 240 s during the reaction. The biodiesel has a higher than conventional method using base catalyst. However, the supercritical methanol method requires a high temperature of 350 °C and a pressure of 45 MPa, and in addition, large amount of methanol is necessary. The comparison of the advantages and disadvantages of each technique are summarized in the Table 4.

Table 4 Comparison of each technology to produce biodiesel

Variable	Alkali catalysis	Lipase catalysis	Supercritical alcohol	Acid catalysis
Reaction temperature(°C)	60 - 70	30 - 40	239 - 385	55 - 80
Free fatty acid in raw material	Saponification productions	Methyl esters	Esters	Esters
Water in raw material	Interference with reaction	No influence		Interference with reaction
Yield of methyl esters	Normal	Higher	Good	Normal
Recovery of glycerol	Difficult	Easy		Difficult
Purification of methyl esters	Repeated washing	None		Repeated washing
Production cost of catalyst	Cheap	Relatively expensive	Medium	Cheap

Source: Marchetti (2007)

The kinetic model of biodiesel formation was proposed by many researches (Freedman *et al.*, 1986; Noureddini and Zhu, 1997; Darnoko and Cheryan, 2000; Foon *et al.*, 2004; Karmee *et al.*, 2004; Vicente *et al.*, 2005; Vicente *et al.*, 2006). The general form of governing differential equations involving three steps is following:

$$\frac{d[TG]}{dt} = -k_1[TG][A] + k_2[DG][E]$$

$$\frac{d[DG]}{dt} = k_1[TG][A] - k_2[DG][E] - k_3[DG][A] + k_4[MG][E]$$

$$\frac{d[MG]}{dt} = k_3[DG][A] - k_4[MG][E] - k_5[MG][A] + k_6[GL][E]$$

$$\frac{d[GL]}{dt} = k_5[MG][A] - k_6[GL][E]$$

$$\frac{d[E]}{dt} = k_1[TG][A] - k_2[DG][E] + k_3[DG][A] - k_4[MG][E] + k_5[MG][A] - k_6[GL][E]$$

$$\frac{d[A]}{dt} = -\frac{d[E]}{dt}$$

where A and E are the alcohol and ester concentrations, respectively.

In addition, the activation energy and reaction rate shown in the Table 5 were estimated by the Arrhenius equation.

$$k(T) = AT^n e^{-E/RT}$$

Table 5 the energy of activation and reaction rate constant at 50 °C

Reaction	Energy of Activation (cal/mol)	Reaction rate constants (L/(mol*sec))
TG → DG	13145	0.05
DG → TG	9932	0.11
DG → MG	19860	0.215
MG → DG	14639	1.228
MG → GL	6421	0.242
GL → MG	9588	0.007

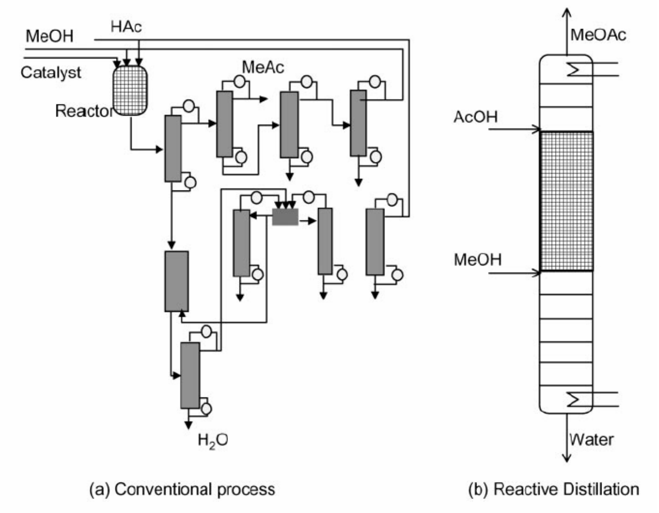
Source: Noureddini and Zhu (1997)

4. Reactive distillation

The reactive distillation is an operation which reactions and separations taking place in the same unit. This technique is especially useful for equilibrium-limited reactions such as esterification and ester hydrolysis reactions. Conversion can be increased far beyond the equilibrium due to the continuous removal of products from the reactive zone. This approach can potentially reduce capital investment and operation costs.

The integration of unit is an interesting**:** (1) simplification or elimination of separation system can lead to capital savings, (2) conversion can be increased by removing production continuously, (3) the azeotropes mixture can prevent by using reactive distillation instead of reactor and distillation. (4) removing one of the products from the reaction mixture can lead to reduction the rates of side reactions and by product formation, (5) if the reaction is exothermic, the heat of reaction can be used to provide the heat of vaporization that reduce the reboiler duty.

As previous mentioned, using the reactive distillation can reduce capital investment such as the production of methyl acetate. The acid catalyst reaction (methanol react with acetic acid to produce methyl acetate and water) was traditionally carried out by using the processing scheme as seen in the Figure 5(a). In this figure, there consists of one reactor and nine distillation. Figure 5(b) shows the reactive distillation implementation, only one column is required. The capital and operation costs are reduced (Siirola, 1995).



(a) Conventional process (b) Reactive Distillation

Figure 5 The Processing scheme for the esterification (a) conventional processing consists of one reactor and nine distillations. (b) The reactive distillation configuration.

Source: Siirola (1995)

For the acid catalyst reaction between iso-bytene and methanol to form methyl tert-butyl ether, the traditional reactor followed by distillation concept has inherently a complexity because the mixture leaving the reactor forms three boiling azeotropes. The reactive distillation implementation requires only one column as illustrated in the Figure 6. The butanes (consists of a mixture of n-butene as non-reactive, and iso-butene as reactive components) and methanol are fed near the bottom of the reactive section. The reactive distillation is capable achiving close to 100% conversion, and suppression of undesired product dimethyl ether (Sundmacher *et al.*, 1995). In addition, some of the azeotrope in the mixture is prohibited (Doherty and Buzad, 1992).

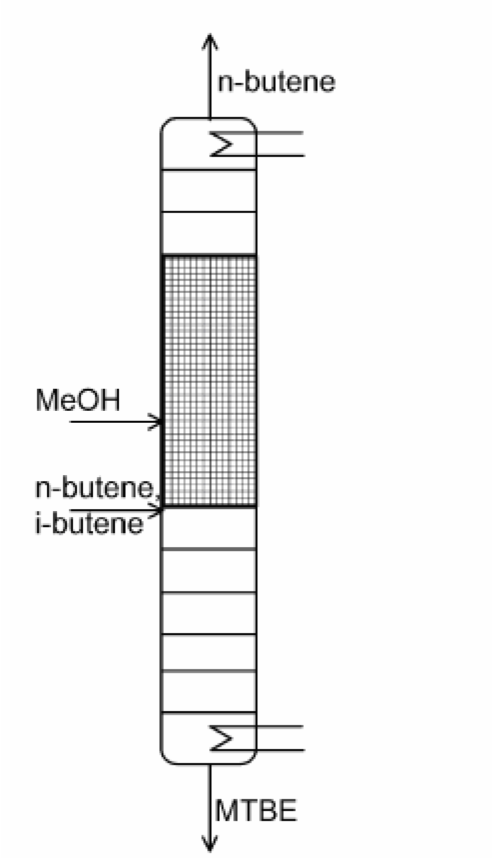


Figure 6 The reactive distillation concept for synthesis of methyl tert-butyl ether.
Source: Sundmacher *et al.*, (1995)

For the hydration of ethylene oxide to mono-ethylene glycerol: EO + $H_2O \longrightarrow$ EG, the reactive distillation in Figure 7 is used for two advantages (Ciric and Gu, 1994). Firstly, the side reaction EO + EG $\longrightarrow$ DEG is suppressed because the concentration of EG is removed continuously. Secondly, the high heat of reaction is utilized to vaporize the liquid phase mixture on the trays. To achieve the same conversion, the conventional plug flow reactor needs at least 60 % excess water (Ciric and Gu, 1994).

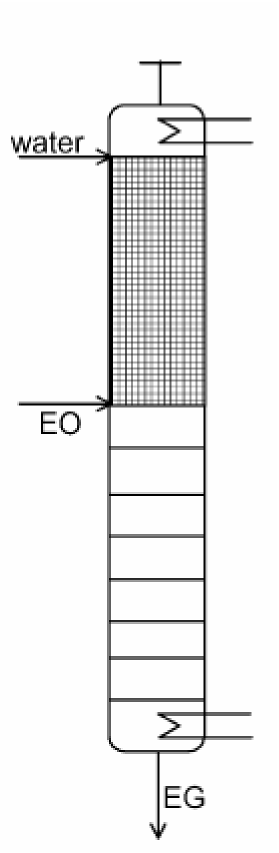


Figure 7 The reactive distillation concept for the hydration of ethylene oxide to ethylene glycerol

4.1 Equilibrium (EQ) stage models

The development and application of the EQ stage model for reactive distillation has been described in several researches (Taylor *et al.*, 1999; Jhon & Lee, 2002; Chen *et al.,* 2003; Pyhalahti, 2005; Alfradique and Castier, 2005; Cheng and Yu, 2005; Katora *et al.*,2005; Dalaouti and Seferlis, 2006; Venkateswarlu and Kumar, 2006;). The equilibrium stage models (Taylor *et al.*, 1999) are demonstrated for calculates the material balances, vapor-liquid equilibrium equations, mole fraction summations and enthalpy balances (MESH).

A schematic diagram of an equilibrium stage is shown in equation 8(a). Vapor from the stage below and liquid from the stage above are brought to contact on the stage together with any fresh or recycle feeds. The vapor and liquid streams leaving the stage are assumed to be in equilibrium with each other. A complete separation process is modeled as a sequence of s of these equilibrium stages (Fig. 8(b)).

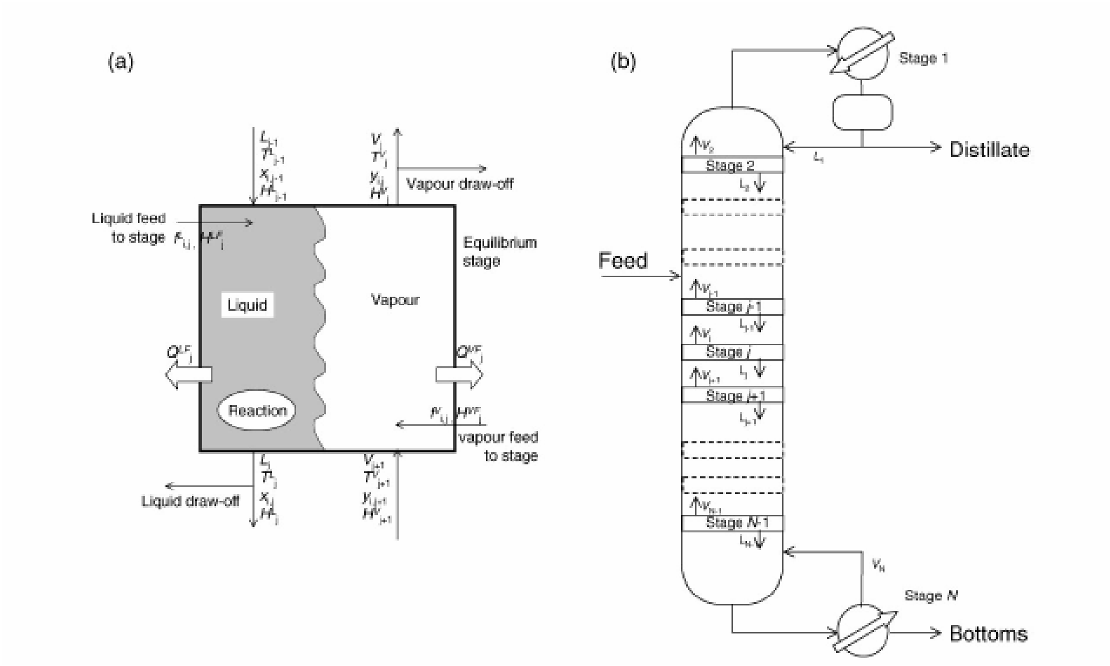


Figure 8 (a) The equilibrium stage (b) Multi-stage distillation column.
Source: Taylor and Krishna, (2000)

4.1.1 The material balance equation (M) is

$$\frac{dU_j}{dt} = V_{j+1} + L_{j-1} + F_j - (1+r_j^V)V_j - (1+r_j^L)L_j + \sum_{m=1}^{r}\sum_{i=1}^{c} \nu_{i,m} R_{m,j} \varepsilon_j \qquad (1)$$

where Uj is the hold-up on stage j. With very few exceptions, Uj is considered to be the hold-up only of the liquid phase. It is more important to include the hold-up of the vapor phase at higher pressures. The component material balance (neglecting the vapor hold-up) is

$$\frac{dU_j x_{i,j}}{dt} = V_{j+1} y_{i,j+1} + L_{j-1} x_{i,j-1} + F_j z_{i,j}$$
$$- (1+r_j^V)V_j y_{i,j} - (1+r_j^L)L_j x_{i,j} + \sum_{m=1}^{r} \nu_{i,m} R_{m,j} \varepsilon_j \qquad (2)$$

In the material balance equations given above r_j is the ratio of side stream flow to inter stage flow:

$$r_j^V = \frac{s_j^v}{V_j}, \qquad r_j^L = \frac{s_j^L}{L_j} \tag{3}$$

$v_{i,m}$ represents the stoichiometric coefficient of component i in reaction m and ε_j represents the reaction volume.

4.1.2 The phase equilibrium equation (E) is

$$y_{i,j} = K_{i,j} x_{i,j} \tag{4}$$

Chemical reaction equilibrium is not considered in many of the early papers because it is more difficult to model.

4.1.3 The summation equation (S)

$$\sum_{i=1}^{c} x_{i,j} = 1, \quad \sum_{i=1}^{c} y_{i,j} = 1 \tag{5}$$

4.1.4 The heat balance equation (H)

$$\begin{aligned} \frac{dU_j H_j}{dt} &= V_{j+1} H_{j+1}^V + L_{j-1} H_{j-1}^L + F_j H_j^F \\ &\quad - (1 + r_j^V) V_j H_j^V - (1 + r_j^L) L_j H_j^L - Q_j \end{aligned} \tag{6}$$

The superscripted H's are the enthalpies of the appropriate phase. The enthalpy in the time derivative on the left-hand side represents the total enthalpy of the stage but, for the reasons given above; this will normally be the liquid-phase enthalpy. Some authors include an additional term in the energy balance for the heat of reaction. However, if the enthalpies are referred to their elemental state then the heat of reaction is accounted for automatically and no separate term is needed.

Under steady-state conditions all of the time derivatives in the above equations are equal to zero.

4.2 Feed location

The optimal feed location was studied by many researches. Luo and Xiao (2001) studied a reactive distillation process for a cascade and azetropic reaction system. They mentioned that the feed locations of the raw materials should have enough contact time for the reactions. The lower boiling point reactant is usually fed in the bottom section of column while the higher boiling point component should be fed in the top. But this general rule is not suitable for the azeotropes system. Cheng and Yu (2005) studied the optimal feed locations of reactive distillation and presented 3 heuristic. Firstly, the heavy reactant should not be fed below the feed tray of light reactant. Secondly, when the relative volatility between the reactant is small, the light and heavy reactant’s feed should be placed close to each other. Similarly, the feed location should be moved away from each other when the relative volatility of the reactant is large. Thirdly, when the relative volatility between the light reactant and the light product is large, the feed location should be in upper part of the reaction zone. On the other hand, if the relative volatility between the heavy reactant and the product is large, the feed location below the reaction zone. In addition, Bhatia *et al*., (2006) studied the production of isopropy palmitate in a catalytic distillation. The heuristics of feed location from Cheng and Yu (2005) were used to study on the conversion and energy saving. The results were good agreement with the heuristic.

4.3 Column pressure

Basically, the operation pressure in the distillation is carried out at the atmospheric pressure. However, there are some cases that operate at low or high pressure (Doherty and Malone, 2001). Low pressure distillation (typically in the range 0.039 – 0.395 atm) is frequently practiced for polymerize or react at normal boiling condition such as acetic anhydride-acetic acid, diketene-acetic acid. High-pressure distillation (typically 3 to 20 atm) is usually occurred when the normal boiling of distillate is lower than the temperature of cooling water. In this case, it is cheaper to pressurize the column in order to raise the boiling point of the distillate that to install a refrigeration system to condense the substance.

However, in the reactive distillation, the operating pressure has affected on the reaction rate and the reaction equilibrium. In case of kinetically controlled and endothermic reaction such as esterification of palmitic acid with isopropanol, operation at the maximum possible pressure is beneficial from the chemical equilibrium and rate of reaction considerations (Subawalla and Fair, 1999). The effect of column pressure was studied by Muhammad (2001) and Bhatia *et al*. (2006). The olefin production was studied by Muhammad (2001). The number of trays, the operating pressure, the hold up per tray and the reflux ratio are studied. The conversion drops after reaching an optimum pressure when the only a small number of tray are used. This is due to the impact of pressure on relative volatilities. In addition, Bhatia *et al*. (2006) simulated the isopropyl palmitate production in a catalytic distillation column. The effects of pressure on the conversion of palmitic acid (PA), the purity of isopropyl palmitate (IPP) and reboiler duty were studied. The increasing of operating pressure raises the reaction rate. When the pressure of column is increased from 1 bar to 3 bar, the PA conversion increases about 3 %. While the IPP purity increases nearly 2 % with the increases of reboiler duty about 34%. However, increasing column pressure makes the higher cost of column.

4.4 Reflux ratio

The reflux ratio is ratio between the amount of reflux that goes back down the distillation column and the amount of product in distillate stream. If no distillate is collected, it is called total reflux ratio. Figure 8 shows the reflux ratio schematic. Normally, reflux ratio is a variable controlling the composition in the over head. The desired separation can be achieved by using a large number of trays but it is a large capital costs. An increasing the reflux ratio, the over head composition can be met the specification by using a fewer number of trays. However, higher energy costs are increased due to increasing utilization of condenser. Figure 9 presents the reflux ratio schematic.

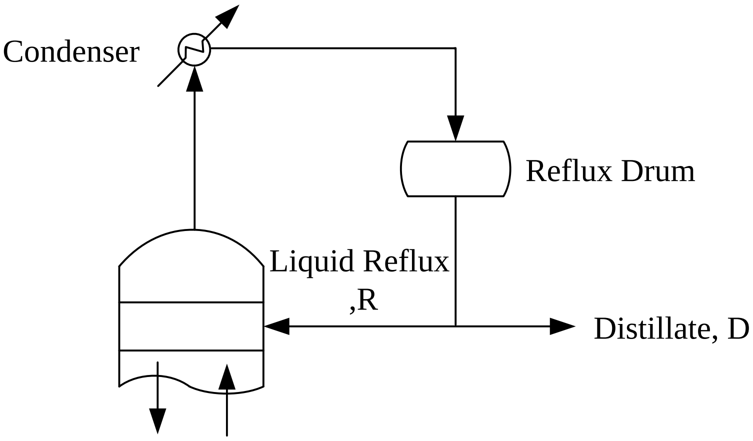


Figure 9 Reflux ratio schematic

In a reactive distillation column, reflux not only enhances the separation but also the reaction by recycling the unconverted reactants to the reaction zone. However, excessive reflux ratio leads to the operating problem and insufficient residence time (Agreda *et al*., 1990; Chopade and Shubham 1997; Luo and Xiao 2001; Bhatia *et al*., 2006). Therefore, the reactive distillation should be operated at an optimal reflux ratio to ensure the good performance and sufficient residence time in the column.