

CHAPTER II

LITERATURE REVIEW

2.1 Background

One hundred years ago, Rudolf Diesel tested vegetable oil as fuel in his engine. Vegetable oils and animal fats were investigated as diesel fuels well before the energy crises in the 1970s. Vegetable oils were also used as emergency fuels and for other purposes during World War II. Besides, concerns about the rising use of petroleum fuels and the possibility of resultant fuel shortages in the United States in the years after World War II played a role in inspiring a “dual fuel” which cottonseed oil or corn oil and blends with conventional diesel fuel were investigated. Moreover, palm oil was often considered as a source of diesel fuel in the “historic” studies; although, the diversity of oils and fats as sources of diesel fuel, an important aspect again today, and striving for energy independence were reflected in other investigations. Recently, increasing of crude oil prices, limiting of fossil fuel oil and environmental concerns have been discussed, resulting in an increased portion of especially on the biodiesel production from vegetable oil and animal oil.

2.1.1 Fuel Sources

Oils, which used to produce biodiesel, come from vegetable oils or animal oils. Those are the renewable oils.

2.1.1.1 Animal Oils

Animal fats are extracted or pressed to obtain crude oil. In beef tallow (Table 2.1), the saturated fatty acid component accounts for almost 50% of the total fatty acids. Most of stearic and palmitic acid contents give beef tallow resulted in the unique properties of high melting point and high viscosity. Animal fats have not been studied in the same extent as vegetable oils due to the limited in chain food of human and animal oils contain more saturated fatty acids than saturated fatty acids which they are solid at room temperature and cannot be used as fuel in a diesel engine in their original form (Ma *et al.*, 2009).

Table 2.1 Typical fatty acid composition-Animal oil source (Kincs, 1985)

Fatty Acid	Lard (%)	Tallow (%)
Lauric	0.1	0.1
Myristic	1.4	2.8
Palmitic	23.6	23.3
Stearic	14.2	19.4
Oleic	44.2	42.4
Linoleic	10.7	2.9
Linolenic	0.4	0.9

2.1.1.2 Vegetable Oils

Vegetable oils are usually triglycerides with different number of carbon into the branched chains, with various fatty acid groups. The advantages of using vegetable oils as fuels are renewable sources, less environmental emissions when compare with fossil fuels, less energy input in production, and nearly competitive with petroleum fuel price (Maher *et al.*, 2006). However, the direct use of vegetable oils or oil blends is generally considered to be unsatisfactory and impractical for both direct-injection and indirect type diesel engines. The high viscosity, acid composition, and free fatty acid content of such oils, as well as gum formation due to oxidation and polymerization during storage and combustion, carbon deposits, and lubricating oil thickening are some of the more obvious problems (Ma *et al.*, 1999; Srivastava *et al.*, 2000; Fukuda *et al.*, 2001). Consequently, considerable effort has gone into developing vegetable oil derivatives that approximate the properties and performance of hydrocarbon-based diesel fuels.

In Thailand, a lot of agriculture oils, for example coconut, soybean, and palm trees, have been planted for an age in order to use for edible oil in household. Majority of oil plants that had grown in Thailand was palm tree because the highest yield per rai of oil was achieved as shown in Table 2.2. However, the gradually expanded harvested area in each year can cause excessive oil in the market. The use of vegetable oils for energy is an opportunity to keep or increase the price of agricultural product.

Table 2.2 Production of vegetable oils in Thailand

Type of Oil	Harvested Area		Production		Yield per Rai	
	(1000 rai)		(1000 tons)		(Kgs)	
	2004	2005	2004	2005	2004	2005
Soybean oil	912	927	218	221	238	238
Peanut oil	250	260	65	67	260	256
Sunflower oil	161	133	49	51	305	385
Palm oil	1,932	2,026	5,182	5,003	2,682	2,469
Sesame oil	398	405	41	42	103	104
Coconut oil	1,590	1,471	1,848	1,674	1,162	1,138
Caster oil	83	83	10	10	118	124

Table 2.3 Chemical structure of common fatty acids (Srivastava *et al.*, 2000)

Fatty Acid	Systematic Name	Structure	Formula
Lauric	Dodecanoic	12:0	C ₁₂ H ₂₄ O ₂
Myristic	Tetradecanoic	14:0	C ₁₄ H ₂₈ O ₂
Palmitic	Hexadecanoic	16:0	C ₁₆ H ₃₂ O ₂
Stearic	Octadecanoic	18:0	C ₁₈ H ₃₆ O ₂
Arachidic	Eicosanoic	20:0	C ₂₀ H ₄₀ O ₂
Behenic	Docosanoic	22:0	C ₂₂ H ₄₄ O ₂
Lignoceric	Tetracosanoic	24:0	C ₂₄ H ₄₈ O ₂
Oleic	cis-9-Octadecenoic	18:1	C ₁₈ H ₃₂ O ₂
Linoleic	cis-9,cis-12-Octadecadienoic	18:2	C ₁₈ H ₃₂ O ₂
Linolenic	cis-9,cis-12, cis-15-Octadecatrienoic	18:3	C ₁₈ H ₃₀ O ₂
Erueic	Cis-13-Docosenoic	22:1	C ₂₂ H ₄₂ O ₂

Vegetable oils are comprised of triglycerides with a number of branched chains of different lengths and notation. Fatty acids have various in

carbon chain length and in the number of unsaturated bonds (double bonds). The structures of common fatty acids are given in Table 2.3.

2.2 Production of Biodiesel

Production methodologies for biodiesel production have been studied such as pyrolysis, microemulsion and transesterification.

2.2.1 Pyrolysis (Thermal cracking)

Pyrolysis, thermal decomposition, is process that converts one substance into another by means of solitary heat or by heat with the aid of a catalyst and involves heating in the absence of air or oxygen. The primary pyrolysis of vegetable oil was conducted in an attempt to synthesize petroleum from vegetable oil since World War I. A large scale of thermal cracking of the tung oil calcium soaps was reported (Chang and Wan, 2006).

Table 2.4 Fuel properties of thermally cracked soybean oil

Properties	Soybean Oil		Cracked Soybean Oil		Diesel Fuel	
	a	b	a	b	a	b
Cetane number	38.0	37.9	43.0	43.0	51.0	40.0
High heating value, MJ/kg	39.3	39.6	40.6	40.3	45.6	45.5
Pour point, °C	-12.2	-12.2	4.4	7.2	-6.7 max	-6.7 max
Viscosity, cSt at 37.8°C	32.6	32.6	7.74	10.2	2.82	1.9-4.1

^a Data from Niehaus *et al.* (1986), ^b Data from Schwab *et al.* (1988).

The cetane number of plant oil is increased by pyrolysis. For example, Soybean oil was thermally decomposed and distilled in air and nitrogen sparged with a standard ASTM distillation apparatus (Niehaus *et al.*, 1986; Schwab *et al.*, 1988).

Cracked soybean oil which is passed pyrolysis has cetane number higher than Crude soybean oil and properties of cracked soybean oil are closely diesel fuel properties (Table 2.4).

2.2.2 Microemulsions

Microemulsion is the formation of thermodynamically stable dispersions of two usually not miscible liquids, brought about by one or more surfactants. Drop diameters in microemulsions generally range from 100 to 1000 Å (Srivastava and Prasad, 2000). The Microemulsion is used to solve the problem of the high viscosity of vegetable oils. microemulsions with solvents such as methanol, ethanol and 1-butanol have been studied (Schwab *et al.*, 1987). They can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles. Moreover, both of ionic and non-ionic microemulsions of aqueous ethanol in soybean oil were nearly as good as diesel. However, microemulsions display considerably lower volumetric heating alcohol value as compared to hydrocarbon-base diesel fuel due to high alcohol contents (Srivastava and Prasad, 2000).

2.2.3 Transesterification (Alcoholysis)

Transesterification or Alcoholysis is the reaction of a fat or oil with an alcohol to form ester and glycerol, as shown in Figure 2.1. The transesterification can be catalyzed by both homogeneous and heterogeneous catalysts. The catalyst is usually used to improve the reaction rate and yield. This reaction is reversible; therefore, excess alcohol is used to shift the equilibrium to the products side. The triglycerides come from vegetable oils or animal fats. The typical alcohols used in transesterification process are methanol, ethanol, propanol, butanol, and amyl alcohol. Normally, methanol is one type of alcohol that is favored for use in this process because of providing a proper viscosity and boiling point, and a high cetane number (Agarwal *et al.*, 2006).

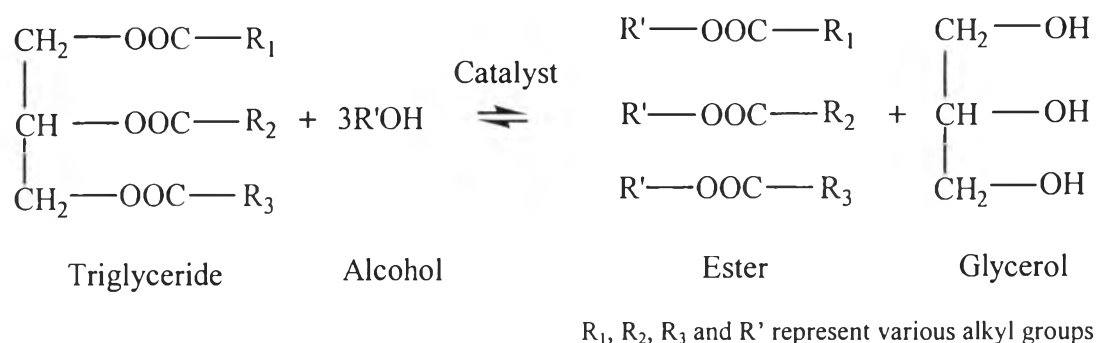


Figure 2.1 Transesterification of triglycerides with alcohol.

2.3 Catalyst

2.3.1 Homogeneous Catalyst

The types of homogeneous catalyses which are used for transesterification are acid or base catalyzed.

2.3.1.1 Acid

Acid catalysis offers the advantage of also esterifying free fatty acids which contain in fats, oils and waste vegetable oil (WVO). Generally, sulphuric acid and hydrochloric acid are used as acid catalysts especially when the oil contains high amount of free fatty acids and water since these catalysts are capable to handle esterification and transesterification of triglyceride simultaneously. Nonetheless, the process requires a high molar ratio of alcohol to oil and long reaction time (Lotero *et al.*, 2005). Besides, under these conditions all the equipment need to withstand against corrosion due to an environmental acidity (Canakci *et al.*, 1999). However, basic catalysts are the most commonly used in industry, because the process proves faster and the reaction conditions are moderated.

2.3.1.2 Base

Normally, NaOH and KOH are examples of homogeneous base catalysts, which are usually used in industrial biodiesel. The transesterification can be performed in a shorter reaction time and relatively modest operation conditions. In spite of this, the water and free fatty acids content in the oil need to be very low because of the probability of soap formation, which can consume catalyst

thus reducing the methyl ester yields. One of the major disadvantages of homogeneous catalysts is that they cannot be reused or regenerated, because the catalyst is consumed in the reaction and separation of catalyst from products is difficult and requires more equipment, which could result in higher production costs.

2.3.2 Heterogeneous Catalyst

There has been increasing interest by many research groups in the use of heterogeneous catalysts due to their many advantages, compared to the conventional process.

In 2005, Xie *et al.* studied the activity of solid base catalysts potassium loaded on Al_2O_3 in methanolysis of soybean oil. They found that the catalytic activities of heterogeneous base catalysts showed a striking correlation with their corresponding basic properties. The decomposition products of the loaded KNO_3 , forming either K_2O species or Al–O–K group in the composite, were probably the active basic sites. In another work, Xie and Li (2006) found that the effect of various types of bases and supports could generate different strong basic sites. Their results demonstrated that the catalyst with 35 wt% KI loading on Al_2O_3 calcined at 500 °C for 3 h was found to be the optimum catalyst, which gave high basic strength, the highest basicity, and the best catalytic activity. Moreover, Li *et al.*, (2007) studied the solid superbase catalyst ($\text{Eu}_2\text{O}_3/\text{Al}_2\text{O}_3$) and its basic strength reached 26.5 measured by indicators. The effects of Europium (Eu) content on the conversion of soybean oil (SBO) increased with increasing basic strength (H_-) of catalyst. At the optimum reaction condition, at a methanol to oil of 6:1 at 70 °C for 8 h, the conversion of soybean oil reached 63%. Furthermore, Kim *et al.* (2004) studied Na/NaOH/ γ - Al_2O_3 heterogeneous base catalyst, which had basic sites stronger than $H_- = 37$, gave maximum biodiesel production yield of 94% at a methanol-to-oil molar ratio 9:1, reaction temperature 60 °C, reaction time 2 h, stirring speed 300 rpm, co-solvent *n*-hexane 10 ml, and loading amount of catalyst 1 g. In addition, the temperature-programmed desorption (TPD) results showed that Na/NaOH/ γ - Al_2O_3 catalyst had stronger base sites than Na/ γ - Al_2O_3 and NaOH/ γ - Al_2O_3 catalysts. On the other hand, three catalysts have nearly the same area of CO_2 desorption peak, implying that the basicity is not much different from each other.

Table 2.5 represents the effect of catalyst precursor by comparing the activity of catalyst with its basic strength and basicity. As can be seen from the table, although the catalysts with high basic strength and the high basicity, less conversion was obtained, which implies that other variables also affect the catalytic activity.

Table 2.5 Effect of precursor type on the catalytic activity

Catalyst	Loading Amount of Active Material (wt%)	Basic Strength (H_-)	Basicity (mmol/g)	Conversion (%)	References
KNO_3/Al_2O_3	35	$15 < H_- < 18.4$	6.75	87	Xie <i>et al.</i> (2005)
KI/Al_2O_3	35	$15 < H_- < 18.4$	1.57	96	Xie <i>et al.</i> (2006)
Eu_2O_3/Al_2O_3	6.75	$H_- = 26$	-	63	Li <i>et al.</i> (2007)
$Na/NaOH/Al_2O_3$	20	$H_- = 37$	-	94	Kim <i>et al.</i> (2004)

However, superbase catalysts are quite expensive and complicated to prepare, which limit their industrial applications. Thus, it is desirable to find more efficient and inexpensive catalysts for the transesterification of vegetable oils in commercial production applications. Zeolite, therefore, has been employed and it was found that the stronger basic zeolites (ETS-10) lead to an increase in conversion and selectivity at the same reaction conditions (Suppes *et al.*, 2004). ETS-10 gave better conversions of triglycerides than zeolite-X-type catalysts, while occlusion of the zeolite-X-type enhanced the activity to levels similar to the ETS-10 at temperatures of around 120 °C for 24 h. These approaches are also reported by using NaX zeolite loaded with KOH as a solid base catalyst, and a conversion of 85.6% was achieved at 120 °C for 8 h (Xie *et al.*, 2007). These studies, nevertheless, have involved high reaction temperatures. The reaction at operation temperatures less than

70 °C has been investigated in a limited number of studies (Maka *et al.*, 2007; Liu *et al.*, 2007). Then, the commercial viability will likely be determined by the costs of the catalysts and useful life of the catalysts.

2.4 Reusability of Heterogeneous Catalyst

Alonso *et al.* (2007) reported the leaching of K/ γ -Al₂O₃ catalyst during transesterification and found that the reduction in catalytic activity took place, yielding 99% of FAME in the first run up to 33% in the second run; 6.5% for the third run, and only 3.8% for the last test carried out. The fresh and spent catalysts were tested by ICP-AES and the K/Al ratio remaining in the solid decreased by 40%, and by 75% in the second and the fourth runs, respectively. These results demonstrate that the decrease in catalytic activity between catalytic runs was due to leaching of active species to the mixture phase. Arzamendi *et al.* (2007) also proposed the reason of leaching of active species that part of the active species initially deposited onto the catalyst is leached from the solids, which reveals a lack of chemical stability of the catalysts under reaction conditions. In addition, Macleoda *et al.* (2008) studied the effects of leaching of the alkali metal dopant (Li, Na, K) on the support of CaO, MgO, and Al₂O₃. They proposed that the loss of metal over time will present some problems since the dissolved metal is catalytically active as a homogeneous part, and the process advantages of the solid catalyst are lost. In the heterogeneous catalysis, it is important to ensure that the active species are not leached from the solid support of the catalyst. If the leaching of the active species on the catalyst is high, the active species could act as a homogeneous part, and the process advantages of the heterogeneous catalysts are lost. Moreover, Meunier *et al.* (2007) reported the deactivation of sulfated zirconia (SZ) after each run. The SZ showed a marked loss of activities from 60 % in the first run to 25% in the second run, and thereafter a slower gradual loss until fourth runs. The leaching of sulfate species was observed and the S content of fresh catalyst was 1.81%, while that of the sample used second and fifth runs were 1.04 and 0.57%, respectively. This observation in Table 2.6 is probably related with the previous literature elsewhere that a significant active species loss has an effect to the activities of catalyst.

Table 2.6 Effect of support type on the amount of active species leaching

Catalyst	Loading Amount of Active Material (wt%)	Amount of Active Species Leaching in First Run (%)	*FAME (%)	References
K ₂ CO ₃ /Al ₂ O ₃	8.75	40	99	Alonso <i>et al.</i> (2007)
NaOH/Al ₂ O ₃	19	<5	96	Arzamendi <i>et al.</i> (2007)
Sulfated zirconia (SZ)	1.81	41.9	60**	Meunier <i>et al.</i> (2007)

*FAME= fatty acid methyl ester or biodiesel, ** Conversion

2.5 Biodiesel Processes

Moreover, the type of reactor is one of the variables in biodiesel production. The biodiesel production between batch reactor and packed bed reactor was compared (Kitakawa *et al.*, 2006). In batch reactor, transesterification catalyzed by the active site of the resin, anion and cation-exchange, was considered. The anion-exchange resins showed a higher activity than the cation-exchange resin. Moreover, the effect of crosslinking, density, and the particle size were investigated and it was found that anion-exchange resin with a lower cross-linking density and a smaller particle size gave a high reaction rate and high conversion, as shown in Table 2.6. In packed-bed reactor, the conversion was found to attain about 120%. It was explained that the impurities of the crude triolein, which used in the experiments were considered to be di- and mono-glycerides bonded linoleic acid group as well as oleic acid group. These impurity components also reacted with ethanol to form fatty acid esters, so that the conversion exceeded 100%. Besides, a heterogeneous catalyst system was developed for the production of biodiesel from used vegetable oil using a continuous process (Park *et al.*, 2008). The pellet-type WO₃/ZrO₂ catalyst showed highly active and durable catalytic activities in the continuous flow process. The steady state conversion of 70% was obtained in a 140 h durability test. Meunier *et al.*

(2007) studied the effect of both batch and packed-bed reactors in term of limited miscibility and mass transfer limitation on the reaction rate. The conversion of both reactors was similar under the optimum condition. While the reaction rate in a batch reactor increased; however, the lifetime of catalyst decreased due to mechanical damage from a stirrer. Therefore, it is an evident that a packed-bed reactor minimizes the rate of catalyst deactivation under the same condition as a batch reactor.

Table 2.6 Effect of reactor type on the catalytic activity

Catalyst	Type of Reactor	Reaction Conditions			Conversion (%)	References
		A	B (g)	C (°C)		
Anion-exchange resin	Batch	10:1	4	50	90*	Kitakawa <i>et al.</i> (2006)
	PBR	10:1	20	50	120	
WO ₃ /ZrO ₂	*PBR	19.4:1	20	200	80	Park <i>et al.</i> (2008)
				75	73	
Sulfated zirconia (SZ)	Batch	9:1	1	60	86	Meunier <i>et al.</i> (2007)
	*PBR				86	

* Packed-bed reactor, A = methanol-to-oil molar ratio, B = amount of catalyst,

C = Temperature

Therefore, many attempts to improve the process for biodiesel production have been ongoing for decades. The ideal process would involve a continuous flow reaction that does not deactivate or consume the catalyst. However, downstream separation and purification steps should be improved for the biodiesel production process.

2.6 Leaching of Active Species from a Heterogeneous Catalyst

Formerly, most of biodiesel research did not concern the reusability or deactivation of a heterogeneous catalyst; however, in the recent research, the influence of the leaching or life time of catalyst with the catalytic activity dramatically requested to discuss in this field. The high amount of leaching would create soluble active species. The leaching of metal, acting as a homogeneous catalyst, result in high conversion instead of catalytic activity of heterogeneous catalyst. The amount of metal leached and catalytic activity of each catalyst was observed as shown in Table 2.7. The order catalytic activity is as follows: $\text{CaO} > \text{FeCl}_3 > \text{Ti}_2\text{O}_3 > \text{ZnO}$. The highest conversion ($> 80\%$) of CaO was achieved due to their highest basic properties. The conversion of Ti_2O_3 and ZnO was sharply increased at temperature over $100\text{ }^\circ\text{C}$, and reached the maximum yield at temperature of $150\text{ }^\circ\text{C}$. The conversion decreased when increasing a reaction temperature owing to cracking of esters at higher temperatures. CaO displayed a different trend to the other catalysts because the conversion of CaO was increased with raising a reaction temperature. It is noteworthy that all of the catalysts described above are capable of elucidating whether there is soluble catalyst. The amount of metal leached over the catalysts is in the following order: $\text{ZnO} > \text{CaO} > \text{FeCl}_3 > \text{Ti}_2\text{O}_3$. The lowest amount of Zn leached from ZnO was observed. Although ZnO has shown awfully soluble solid in solution, this property is necessary for the heterogeneous catalyst. Di Serio *et al.*, (2010) discussed that the leaching of TiO_2 content on the exhausted catalyst, reducing from 5.3 to 2.0 %, is due to the solubility of titanium at high temperature in methanol phase. This solubility is very low because the concentration of titanium in methanol after the reaction is less than the sensibility of the UV method (5×10^{-5} mol/L) and a very low equilibrium value of titanium in the solution is achieved. Moreover, authors have identified the level of soluble species in their reaction that it could not influence on the FAME as a homogeneous did, and it did not disturb some remained active sites on supported sites. Further, Jin *et al.*, (2011) studied $\text{La}_2\text{O}_2\text{CO}_3$ modified by loading ZnO. They found that high catalytic activities were achieved with no leaching into the reaction medium. Nevertheless, conversion still decreased from 98% in the 1st run to 75% FAME yield in the 4th cycle, this might be due to the

loss of catalyst during the re-collection and reactivation process. As the matter of fact, catalysts classified as heterogeneous are not observed or rarely found the leaching of metal in the presence of product.

Table 2.7 Conversion and amount of leached active species of a heterogeneous catalyst

Catalyst	Reaction Conditions				Leaching of Metal (ppm)	Conversion (%)	References
	A	B (g)	C (°C)	D (bar)			
ZnO					155	50	
CaO	7:1	2	150	No report	8300	80	Singh <i>et al.</i> (2008)
Tl ₂ O ₃					54000	78	
ZnO	30:1	10	220	55	0.1	20	Di Serio <i>et al.</i> (2010)
FeCl ₃					32000	85	
CaO	13.4:1	13.78	60	0	22192	98	Fu <i>et al.</i> (2011)
ZnO/ La ₂ O ₂ CO ₃	28:1	5	85	No report	No leaching	95	Jin <i>et al.</i> (2011)

A = methanol-to-oil molar ratio, B = amount of catalyst, C = Temperature, D = Pressure

2.7 Properties of Materials

2.7.1 Alumina

Aluminas, Al_2O_3 , are the most widely used material in the industrial engineering ceramics. The surface chemistry of alumina plays an important role in their performance as catalysts and catalyst supports. Many aluminas are prepared by loading other chemical species. Alumina supported by alkaline as an effective solid catalyst is used to promote base-catalyzed reactions, for example, KF, KOH, and KNO_3 . On the other hand, acid-catalyzed reactions, such as alcohol dehydration, esterification, etherification, and dealkylation of alkylbenzenes, were prepared by promoting alumina with phosphate or sulfate, and niobium phosphate (Abdel-Rehim *et al.*, 2006).

2.7.2 NaY Zeolite

NaY zeolite displays the FAU (faujasite) structure as shown in Figure 2.2a. It has a 3-dimensional pore structure with pores running perpendicular to each other in the x, y, and z planes. The largest pore diameter is 7.4 Å since the hole is classified by a 12 member oxygen ring. Moreover, Si/Al ratio of zeolite Y is in the range of 3-5. The cavity is surrounded by ten sodalite cages connected on their hexagonal faces. Generally, a key fraction of the ion-exchanged cations is in the hexagonal prism and in the sodalite cage (Thoret *et al.*, 1997).

2.7.3 Na-mordenite Zeolite

Mordenite is one of the most abundant zeolites. The framework of mordenite contains chains of five-membered rings of linked silicate and aluminate tetrahedra (four oxygen atoms arranged at the points of a triangular pyramid about a central silicon or aluminium atom) as shown in Figure 2.2b. Its high ratio of silicon to aluminum atoms ($\text{Si/Al} = 8-12$) makes it more resistant to attack by acids than most other zeolites (Groen *et al.*, 2007). Like the NaY zeolite, mordenite has an ability to exchange ion with many cations such as K, Rb, Cs, Ca, or Mg etc.

2.7.4 Bentonite Clay

The use of bentonite in numerous applications is needed for paints, pharmaceutical and cosmetic uses, waste disposal, lubricants, additives for cement and mortar, catalysts and catalyst supports, and other miscellaneous applications. Bentonite is comprised of hydrated aluminosilicate (Si_2O_5) layer of SiO_4^{2-} tetrahedrons joined with $\text{AlO}(\text{OH})_2$ layer of octahedral arrangement of O and OH around the Al. Layers connected by O^{2-} ions which are shared by each layer. Substitutions of another ion such as Mg^{2+} with Al^{3+} in the octahedral layer give the layer an overall negative charge. Insertion between layers by cations, for example, Ca^{2+} , K^+ , Na^+ to balance negative charges on each layer as shown in Figure 2.2c (Wypych and Satyanarayana, 2004).

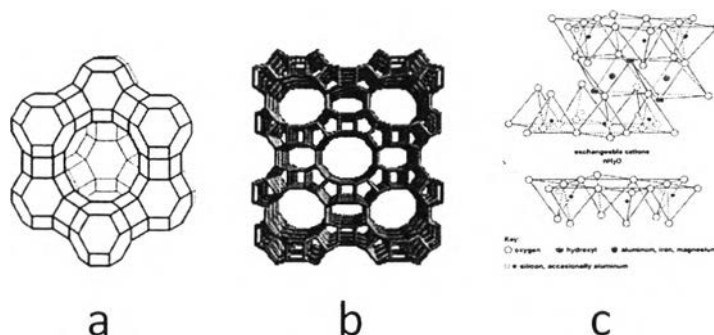


Figure 2.2 Framework structure of a) NaY zeolite, b) mordenite, and c) bentonite clay.