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A review of the synthesis and characterisation of pillared clays and related porous materials for cracking of vegetable oils to produce biofuels

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Abstract This paper presents an overview of the modification of clay minerals by propping apart the clay layers with an inorganic complex. This expanded material is converted into a permanent two-dimensional structure, known as pillared clay or shortly PILC, by thermal treatment. The resulting material exhibits a two-dimensional porous structure with acidic properties comparable to that of zeolites. Synthetic as well as natural smectites serve as precursors for the synthesis of Al, Zr, Ti, Fe, Cr, Ga, V, Si and other pillared clays as well as mixed Fe/Al, Ga/Al, Si/Al, Zr/Al and other mixed metal pillared clays. Biofuels form an interesting renewable energy source, where these porous catalytically active materials can play an important role in the conversion of vegetable oils, such as canola oil, into biodiesel. Transesterification of vegetable oil is currently the method of choice for conversion to biofuel. The second part of this review focuses on the catalysts and cracking reaction conditions used for the production of biofuel. A distinction has been made in three different vegetable oils as starting materials: canola oil, palm oil and sunflower oil.

Key words: Canola oil, Cracking reaction, Pillared clay, PILC

Introduction

Escalating crude oil prices and environmental awareness have increased interest in the use of renewable fuel sources. One area of attention is the upgrading of vegetable oils for use as a fuel or fuel additive. Besides being a renewable source, the use of vegetable oils has benefits economically and environmentally. Such oils are CO₂ neutral and contain little, if any sulfur, nitrogen and metals, which are major pollutants in current fuel emissions (Katikaneni and others 1998). The possibility also exists for the reuse of current vegetable oil wastes such as wastes from fast food restaurants. As such, oils come from plants that can be easily grown; its production can be localized and adjusted according to demand. The conversion of the oil to fuel can therefore bring benefits to the community economically as well as making them no longer reliant on outside sources.

Over the years, vegetable oils have been substituted for diesel for use in engines but this has led to problems such as carbon deposits, oil ring sticking and gelling of the lubricating oil (Ma and Hanna 1999). Because of such problems, research in this area has been centered on the conversion of these oils to a form that is similar to current fuels. One such fuel, which is currently gaining much attention, is biodiesel. This is a variety of ester-based oxygenated fuels made from vegetable oils or animal fats.

There are several methods for the conversion of vegetable oils to biodiesel of which the most common is the transesterification process, in which an alcohol is reacted with the oil to form esters and glycerol (Ma and Hanna 1999). The esters are separated and commonly used as a mixture with petroleum diesel (20:80) to minimize engine modification requirements. Altin and others (2001), showed that vegetable oil methyl esters gave performance and emission characteristics close to petroleum diesel. The main problems associated with the increased use of this fuel are the costs of the oil and its processing. Also, the marketing of this product is limited to diesel engine applications.

Another method for the conversion of vegetable oils to a useable fuel product is by catalytic cracking reactions. This is currently used in the petroleum and petrochemical industry to convert high molecular weight oil components to lower molecular weight ones which can be used directly or blended for use as fuel (Thomas

and Thomas 1997). The reaction process usually involves the mixing of catalysts with the oil feed at high temperature in a fluid catalytic cracker (FCC) unit. Here the hydrocarbon product is collected and the spent catalyst is directed to a regenerator which oxidizes the coke that has collected on it, to CO, CO₂ and H₂O, to then be reused (Venuto and Habib 1979).

Acid-treated clay of the montmorillonite type was the catalyst commonly used for initial cracking reactions in the 1930s (Thomas and Thomas 1997). Such catalysts were replaced after World War II with a more stable synthetic silica-alumina type which also gave better product distribution (Thomas and Thomas 1997). The emergence of zeolites in the 1960s revolutionized the process mainly because of their high activity, selectivity and resistance to collapse when treated at high temperatures (Venuto and Habib 1979). Their use is commonplace now with ZSM-5 and Y types being some of the most popular catalysts. The interest now is in producing a catalyst with a larger pore size compared to zeolite (~8 Å) to handle the cracking of heavier crude oil. The use of pillared clays has received considerable attention because of their ability to achieve large pore sizes, but factors such as thermal stability and coking properties still need to be overcome.

It is common knowledge that vegetable oils can be cracked into lighter fuel fractions by the use of such catalysts. There are, however, a number of problems associated with this process with cost being one of the major ones. Altin and others (2001) noted that at present vegetable oils are more expensive than diesel fuels. However he suggests that with an increase in consumption should come an increase in production and this would lead to more mechanised farming methods which would probably translate into a decrease in cost.

Another problem with the use of vegetable oils for conversion to fuels is that the composition of such oils varies drastically between types. This means that a particular set of reaction conditions and catalyst type will give different products according to the starting oil.

Smectites

Clays are phyllosilicates or layer silicates with a layer lattice structure in which two-dimensional oxoanions are separated by layers of hydrated cations. The oxygen atoms define upper and lower sheets enclosing tetrahedral sites and a central sheet having the brucite or gibbsite structure enclosing octahedral sites. Smectites have two tetrahedral sheets around the central octahedral sheet in each layer, hence the name 2:1 phyllosilicate. These layers have a positive charge deficiency resulting from isomorphous substitutions (e.g. Si^{4+} by Al^{3+} at tetrahedral sites or Al^{3+} by Mg^{2+} at octahedral sites). These negative layer charges are balanced by exchangeable hydrated interlayer cations such as Na^+ , K^+ or Ca^{2+} . The charge deficiency and the origin of this deficiency (octahedral vs tetrahedral) result in different physical and chemical properties, such as, thermal stability and swelling behaviour. Layer charges related to tetrahedral substitutions lead to a localised charge distribution, while layer charges related to octahedral substitutions are more distributed over the complete oxygen framework.

Pillared Interlayered Clays (PILCs)

As a consequence of increasing oil prices, PILCs were improved in the mid-1970s to optimise the catalytic cracking of crude oil. To increase the yield of lighter fractions from heavy crude oil, catalysts were required that had larger pore size and good thermal and hydrothermal stability (Ding and others 2001; Frost and others 1998; Kloprogge 1998). This was research focussed on the use of inorganic hydrated polyoxocations as pillaring agents. Such pillaring agents, when calcined, dehydrate and dehydroxylate to form a fixed metal oxide pillar with a high thermal stability and high surface area. The use of the Al_{13} polyoxocation was favoured as it had been extensively researched and reported previously and was easily prepared (Gil and Gandía 2000).

The first step in the pillaring process is to prepare a pillaring agent. In the case of the Al_{13} polyoxocation, two methods are commonly used: 1) mixing of aqueous AlCl_3 with Al to form a chlorohydrate which is also commercially available, and 2) addition of a base to AlCl_3 or $\text{Al}(\text{NO}_3)_3$ solutions with OH/Al^{3+} ratios up to 2.5. The

polyoxocation complex produced has been analysed and is thought to be the tridecamer $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$, also referred to as the Keggin ion (Kloprogge 1998; Kloprogge and others 1992).

The next step is the mixing of a clay suspension with this polyoxocation solution. This allows the interlayer cations in the clay to exchange with the polyoxocation in solution through *cation exchange reaction* or *intercalation* (Gil and Gandía 2000). After the intercalation process is complete, the clay is separated, washed and then calcined. The property of the stable pillared structure obtained is greatly affected by factors such as clay used, mixing and drying conditions and polycation/s used.

Vegetable oil

Vegetable oils are predominantly made up of triacylglycerols with a small amount of minor compounds (2-5%) (Cert and others 2000). Triacylglycerols are made up of one glycerol molecule joined to 3 fatty acids by an ester link. As shown in Figure 1, the type and concentration of fatty acid varies considerably from one vegetable oil to another. Hence, it is important to be aware of the composition of the vegetable oil used for the choice of the catalyst, as it will determine the type of reactions that are probable. The four major vegetable oils produced today are palm oil, soybean oil, sunflower oil and rapeseed oil. The production of palm oil has increased at a great rate over the past 5 years. One report estimates that the world trading of palm oil has grown 32% since 1997-98 (Anonymous 2001). This has led to a decrease in prices with the Malaysian average palm oil prices in 1999-00 falling to \$314 per metric tonne a decrease of around 35% from 1998-99 (Guzman 2001). This reduction in price and high availability makes it ideal as a fuel source.

Oil is extracted from the fruit of the oil palm which is usually grown in areas within 10° of the equator (Gunstone and Society of Chemical Industry (Great Britain) 1987). It produces two types of oil, one from the flesh (palm oil) and another from the kernel (palm kernel oil) of the fruit. These oils can then be separated into a high-melting fraction (stearin) and a low-melting fraction (olein) (Gunstone 1996). The yield is about 4-5 tonnes/hectare of palm oil and 0.5 tonnes/hectare of palm kernel oil.

The main use of soybean is the protein rich meal obtained after extraction of the oil. This is used for animal feed and makes up between 50-70% of its value (Gunstone 1996). Soybean oil prices are currently at the lowest they have been since 1986-87 (Guzman 2001). It is mainly produced in USA, China, Brazil and Argentina (Gunstone 1996). Soybean oil is highly unsaturated with linoleic and linolenic acid comprising over 60%. The remainder is predominantly oleic and palmitic acid. The sunflower plant is mainly grown in the former Soviet Union, the European Union, Argentina, China, USA, and Eastern Europe (Gunstone 1996). It too is at its lowest price since 1986-87 (Guzman 2001). The seed oil is also highly unsaturated, containing mostly linoleic and oleic acid.

Rapeseed oil source has received the most attention with considerable research performed on the altering of the plants by breeding techniques and genetic modification. Such changes have been made to give the plant specific qualities such as tolerance to broad-spectrum herbicides (Friedt and Lühs 1998). The project is of interest for the possibility of modifying the fatty acid composition of the oil by using these techniques. Not only can the length of the fatty acid be altered, but also properties such as the degree of unsaturation, stereochemistry and position of double bonds (Friedt and Lühs 1998). It may be possible therefore to modify the plant to grow in a particular climate and produce oil that has the properties necessary for optimum cracking reactions.

According to Friedt and Lühs (1998), rapeseed oil is ideal for non-food applications because of qualities such as relatively homogeneous composition, high degree of refinement, freedom from contaminants and also biodegradability. This is evidenced by the relatively large number of studies that have used canola oil, a modified rapeseed oil, to investigate cracking reactions.

Unmodified rapeseed oil is high in erucic, oleic and linoleic acid. The composition varies greatly among plant variety with some oil products being high in the saturated lauric acid. It is mainly produced in northern Europe, China, India and Canada. Australia has recently increased its production with estimates of about 300,000 tonne now achieved annually (Department of Natural Resources and Environment 2001).

Although coconut oil is not produced on as large a scale as the oils mentioned previously, it would be of interest to study the cracking reactions associated with this oil as it is quite high in lauric acid. This makes it highly saturated oil and it would be expected that any major differences in reaction products could be largely attributed to this fact.

Pillared clays as cracking catalysts

As noted previously, a major problem associated with the use of pillared clays as catalysts has been their lack of thermal and hydrothermal stability above roughly 600 to 700°C depending on the pillar and clay used. Because of this, many studies have focussed on methods of improving such stability while also retaining, or increasing, its catalytic properties. Current research has examined how the introduction of various pillaring species alters the PILC properties (see e.g. review Kloprogge 1998). Another way of changing the property of PILCs has been to alter preparation techniques. This is usually examined after the pillaring species has been optimised so as to maximise the desired properties of the PILC. Each method has had various degrees of success and will be further discussed.

Various pillaring species

This usually involves intercalation with one easily pillared cation, such as Al, and then the addition of another cation to give the PILC a specific property. Some cations that are used are Ce, Cr, Ga, La, Si, Ti, and Zr. Because there are a large number of cations available, extensive study has been carried out in this area and a few will be discussed here for an overview.

Gallium

This cation has a number of chemical properties (eg. ionic radius) that are similar to Al^{3+} , making it ideal for pillaring. Bradley and others (1990a) have shown that the Ga_{13} and GaAl_{12} pillaring agents that can be formed by hydrolysis, are similar in structure to the Al_{13} Keggin-ion species. The d_{001} spacing of the Ga_{13} species was around 5.6% larger than Al_{13} . This correlated well with their estimate of 5.7% for a

Keggin-like structure. The pillaring solutions prepared were tested for thermal stability by allowing each to reflux until a precipitate formed. It was found that the GaAl₁₂ solution could be refluxed for over 3 weeks, over 5 times longer than the Al₁₃ solution. Using NMR techniques, such stability was attributed to the overall increase in symmetry of the pillar owing to the better fit of the Ga³⁺ ion in the central position of the modified Keggin structure (Bradley and others 1990b). Further MAS NMR, IR and XRD studies confirmed that the GaAl₁₂ structure is structurally analogous to the Al₁₃ species (Bradley and others 1992, 1993).

Bradley and Kydd (1991) were also able to demonstrate how the thermal stability of the GaAl₁₂ PILC was markedly better than Al₁₃ and Ga₁₃. They found that the surface area of the GaAl₁₂ pillared clay dropped from 277 to 196 m²/g over a temperature range of 200 to 700°C whereas the other two PILCs dropped to less than 115 m²/g. This correlated with the stability of the ions in solution. In a further article they examined the Brønsted acidic character of these pillared clays and concluded that the GaAl₁₂ pillared clay had the highest abundance (Bradley and Kydd 1993).

González and others (1992) also produced thermally stable GaAl PILCs that retained 70% of its surface area when heated to 700°C. In a later study (Hernando and others 1996), they examined how modifying this PILC with cerium effected its thermal stability and catalytic properties. They determined that although the presence of Ce decreased the surface area of the PILC, it also increased the Brønsted acid site density making it more selective toward cracking reactions.

González and others (1999), also studied the catalytic properties of GaAl PILCs with respect to the cracking of heavy oils. They produced thermally stable PILCs that retained around 85% of its surface area and micropore volume when heated to 700°C. As shown in Table 1, the GaAl PILC was the only one to exhibit a basal spacing by XRD at 700°C (17.3 Å). The results from their fixed-bed reactor at 482°C indicated that, although the GaAl PILC had the highest activity, it formed more gaseous product and had a higher coke formation than the Al PILCs. The gasoline product formed by the GaAl PILC did however have a higher octane number, which somewhat compensates for lack of quantity. This higher octane number was

attributed to the dehydrogenating effect of the Ga, which resulted in the production of more alkenes.

Lenarda and others (1999) also produced PILCs using a solution containing an Al/Ga ratio of 12/1. They further treated the PILC with NH₃ vapours and repeated the pillaring process. The re-pillared clays had a similar XRD pattern to the standard PILC but had a decrease in surface area from 383 to 323 m²/g and an increase in pillar density of 30%. This was due to the re-pillaring process in which more pillars diffuse into the interlayer space and/or unpillared or partially pillared areas are completed (Fig. 2). They too found that the GaAl₁₂ species retained its structure up to 700°C.

Domínguez and others (1998) examined the hydrolysis of various mixed solutions and concluded that for the Al-Ga system, the formation of GaAl₁₂ species was more probable in the pH range of 4 - 5, after which the Al₁₃ species was more likely to form.

Lanthanum and Cerium

Sterte (1991) assessed lanthanum as a rare earth cation that, "most readily formed a complex with aluminium suitable for pillaring". This author was able to produce LaAl pillared montmorillonite with basal spacings of around 26Å and surface areas of 300-500 m²/g. The pillaring solution was prepared by either refluxing mixtures of aluminium chlorohydrate and lanthanum chloride for up to 120 hours or by treating the solution in an autoclave at 120°-160°C for 12-96 hours. He determined that a La/Al ratio of at least 1/5 was needed to produce large pore structures. From XRD analysis it was shown that between 72 and 96 hours of refluxing was required for maximum basal spacings while only 12 hours was needed for solutions autoclaved at 160°C.

Booij and others (1996) also attained, by hydrothermal treatment, large pore LaAl and CeAl PILCs with basal spacings around 25Å and surface areas of about 430m²/g. They concluded that the La/Al or Ce/Al molar ratio can be as low as 1/30 as the formation of the initial polyoxocation is favoured by high Al concentrations. They attributed the stability of the pillared structure to the higher Al^{tetrahedral}/Al^{octahedral} ratio compared to the normal Keggin structure.

Valverde and others (2000) synthesized PILCs by mixing 0.05M solutions of $\text{La}(\text{NO}_3)_3$ or $\text{Ce}(\text{NO}_3)_3$ with a bentonite clay suspension that had already been allowed to react with an Al polyoxocation solution. Basal spacings of 16 to 20 Å were recorded with surface areas from 239 to 347 m^2/g . Although these pillared clays were similar in structure and acid properties to Al PILCs, they showed an increase in thermal and hydrothermal stability. They concluded that the cations were not part of the pillar and that they delayed the dehydroxylation of the PILC with Ce being more effective than La. They suggested that this delaying effect was due to the cation either blocking the hexagonal cavities in the tetrahedral layer or somehow strengthening the bonding of the Al pillars.

Various montmorillonites from different localities were pillared with Ce and Al by Pires and others (1998). They found that by changing the total metal concentration of the pillaring solution they could regulate the interlayer pore size. Basal spacings up to 22.2 Å were recorded at 500°C with specific surface areas being as high as 300 m^2/g at 700°C. They observed that the extent of octahedral substitution in the parent clay had a large influence on the thermal stability of the PILC produced.

Silicon

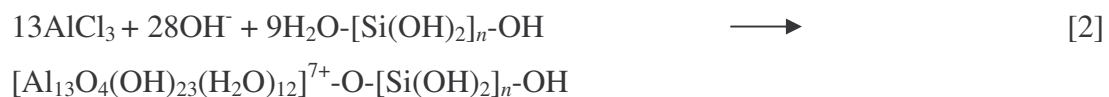
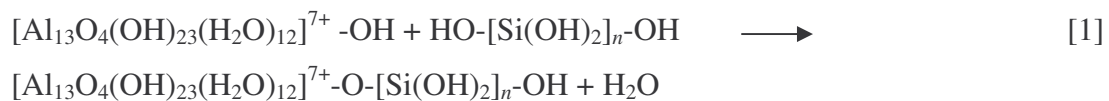
By using two industrially produced silanes, 3-aminopropyltrimethoxysilane (APTMS) and 2-(2-trichlorosilylethyl)pyridine (TCSEP) as pillaring solutions, Fetter and others (1994) were able to produce pillared clays having good thermal stability. The PILC intercalated with TCSEP gave a number of interlayer spacings (up to 10 Å), which were attributed to the range of polymeric species present in the solution. It had however, poor thermal stability with its structure almost collapsing at 700°C. The use of APTMS gave a more homogenous interlayer spacing of around 7 Å and was stable up to 700°C. This PILC also maintained a large microporosity and some acidity at 700°C. A further study (Fetter and others 1995) used competitive ion exchange of Al-polyoxocations and TCSEP to produce a pillared clay exhibiting good thermal stability with an acidity comparable to that of HY zeolites. The SiAl PILC produced had a basal spacing of 17.4 Å and a surface area of 278 m^2/g when calcined at 600°C (the temperature necessary to burn off the organic moiety). With further calcination at

700°C, the surface area only decreased to 244 m²/g with a basal spacing of 17.2Å.

XRD patterns showed that the structure collapses at around 800°C.

Sterte and Shabtai (1987) produced hydroxy-SiAl pillaring solutions by two methods: (1) by mixing orthosilicic acid with AlCl₃ and then treating with aqueous NaOH and allowing to age and (2) by ageing an Al₁₃ solution and then combining with orthosilicic acid. The SiAl pillared montmorillonite produced by the first method gave basal spacings around 19Å (table 3) and were not affected by the Si/Al ratio in the pillaring solution. The surface area did drop substantially as the Si/Al ratio increased. The same trend occurred for the PILCs prepared by the second method except the basal spacings were lower (~17Å). The decrease in surface area was attributed to the increase in substitution of -OH groups by the bulkier -OSi(OH)₃ groups in the pillaring species. They also examined the thermal stability of the PILCs and noted a rapid decrease in surface area for Si/Al ratio of 0.53 as it was heated to 600°C whereas it was slower for Si/Al ratios of 1.04 and 2.08.

Zhao and others (1992) also prepared SiAl PILCs by methods similar to Sterte and Shabtai (1987) and they found that the structure of the PILCs produced by both methods were similar but the SiO₂ content of the PILC produced by method (2) was higher than that from method (1). This led them to likewise conclude that Si was incorporated into the Al pillars and ²⁷Al-NMR was used to confirm that the pillar structure was similar to the Keggin structure in Al PILCs. Hence, they suggested two reactions occurring in solution:



Thus a structure was proposed similar to that of Sterte and Shabtai (1987) and is depicted in Figure 3. Sterte and Shabtai (1987) also found that the SiAl PILCs had more Brönsted and Lewis acid sites compared to Al-pillared species and a lower

Lewis/Brønsted ratio. This was attributed to the presence of acidic silanol groups in the pillars. The cumene cracking ability of the SiAl PILC was examined and they found an increase in activity due to the incorporating of silica into the aluminium pillars.

Zirconium

Farfan-Torres and others (1992) describe two methods of preparing Zr PILCs. Both methods involve the mixing of zirconyl chloride (ZrOCl_2) solution to a clay suspension with one having an extra step of refluxing at 100°C to force polymerization of the Zr complex. The non-refluxed solution produces a square planar complex that can then polymerize to give Zr_8 and Zr_{12} units and upon calcination at 500°C , give PILCs with basal spacings of 16\AA . This method has the disadvantage of being time consuming whereas the refluxed solution is quicker but produces PILCs with disordered layer structure and basal spacings around 15\AA . This led them to investigate how parameters such as time of reaction, temperature of reaction and concentration all affect the degree of polymerization. They found that although heating of the ZrOCl_2 solution and higher contact time assisted the polymerisation process, it also causes the pH to drop which led to degradation of the clay structure. The pH drop is due to the zirconyl ion, present as the tetramer $[(\text{Zr}(\text{OH})_2 \cdot 4\text{H}_2\text{O})_4]^{8+}$, hydrolysing to form the tetramer $[\text{Zr}_4(\text{OH})_{14} \cdot 10\text{H}_2\text{O}]^{2+}$ and H^+ . Although the authors do not examine the stability of the pillared clay above 500°C , they do show that the introduction of Zr enhances the acidic properties of the solid. Ohtsuka (1993) intercalated sodium fluoride tetrasilic mica with ZrOCl_2 solutions of various concentrations at room temperature and at an elevated temperature. He produced intercalated clays having interlayer spaces of 7, 12 and 14\AA according to the degree of polymerization of the zirconium tetramer. The dimension of this tetramer was given as 8.98\AA wide and 5.82\AA thick. This was given as the major species responsible for producing the 7\AA interlayer distances with two and three two-dimensional layers being responsible for the 12 and 14\AA species respectively. Halogens in solution (Cl^- , Br^-) were shown to form part of the zirconium tetramer and, if present in high concentrations, had an effect on the extent of polymerisation. The PILC formed from the 14\AA species has an homogenous pore structure and

exhibited good thermal stability with the interlayer spacing falling to only 10 Å upon heating to 700°C and the surface area reaching a maximum at 600°C.

Gandía et al. (1999) pillared saponite and montmorillonite using, what they term, a non-aggressive method in which a commercial solution of zirconium in acetic acid was used. The intercalation step was performed with pH=3.3 at room temperature while the calcination was performed at 500°C. This method produced basal spacings of 14-24 Å with surface areas up to 300 m²/g. In a further study (Gill and others 2000), they found that upon calcination the Zr PILC actually increased in surface area. This increase was attributed in part to the decomposition of acetate ligands thus giving access to the porous network of the PILC.

A comparison of the properties of the Zr PILC to the ZrAl species was made by Cañizares and others (1999). They prepared the Zr-PILC using a ZrOCl₂ solution mixed with bentonite. They tried three methods to produce the ZrAl PILC: (1) impregnating an Al-PILC with Zr, (2) mixing the ZrOCl₂ solution to previously intercalated Al clay slurry and (3) mixing of Al and Zr pillaring solutions, addition of a basic solution to give OH/Al ratio of 2 and then ageing for 16 hours. The first method gave products which could not be calcined higher than 200°C before structural collapsed. The products of the second method could be calcined successfully but resulted in low basal spacings. The third method gave acceptable PILCs and was used for further analysis. They only analysed the PILCs up to 500°C but were able to conclude that, “the surface acidity, methane adsorption and thermal stability were increased by incorporating aluminium into the single oxide pillars”. It was also shown that the structure of the pillar varied with Al concentration with the Keggin structure predominating at higher Al/Zr ratios.

Chromium

A solution of CrCl₃ and AlCl₃ in Na₂CO₃ was used by Zhao and others (1995) to produce a CrAl PILC. Basal spacings of around 18 Å were achieved when calcined at 500°C with surface areas around 230 m²/g. The thermal stability was found to be greater than that of Cr PILC as well as possessing more acid sites. Toranzo and others (1997) stated that Cr³⁺ can form the trimer [Cr₃(OH)₄(H₂O)₉]⁵⁺, the dimer [Cr₂(OH)₂(H₂O)₈]⁴⁺ or no polymerization occurs depending on the Al³⁺/Cr³⁺ ratio in

the solution. They also found that CrAl PILCs were more stable thermally than Cr PILCs.

Titanium

Del Castillo and Grange (1993) determined that $\text{Ti}(\text{OEt})_4$ (titanium tetraethoxide) gave a polycationic precursor that gave a PILC of regular structure and was stable at 600°C . Regulating the pillar size and distribution was difficult as it depended greatly on solution pH and reaction temperature. The acidity of the Ti PILCs produced were determined to be mainly of the Lewis kind.

Swarnakar and others (1996) prepared a TiAl pillaring solution by hydrolysis of AlCl_3 and $\text{Ti}(\text{OEt})_4$ for pillaring of beidellite and montmorillonite. From XRD analysis it was determined that the pillared beidellite was thermally more stable than the pillared montmorillonite with a peak seen at 700°C .

Tantalum

The intercalation of montmorillonite using niobium and tantalum was performed early on by Christiano and others (1985). They produced PILCs with basal spacings around 18 \AA but they were only stable to 400°C . Guiu and Grange (1994, 1997) examined ways to produce more stable Ta PILCs. They prepared a pillaring solution by controlling the hydrolysis of $\text{Ta}(\text{OC}_2\text{H}_5)_5$ in an ethanolic acidic solution. The PILC had a basal spacing of 26 \AA and was stable to 600°C . A pillar precursor structure was proposed as $[\text{Ta}_8\text{O}_{10}(\text{OR})_{20}]$, $\text{R} = \text{H}, \text{C}_2\text{H}_5$. The pillaring of Ta was shown to produce stronger Lewis sites and new Brönsted sites.

Preparation techniques

Altering the preparation of a PILC can have dramatic effects on properties such as thermal stability and acidity. This area also has received considerable attention with many authors who are looking at ways to economise the process for commercial viability. Current problems in preparation are time and energy costs, water usage and mixing of clay solutions. Some of these issues, along with property changes, have been addressed and will now be discussed briefly.

Intercalation step

Mixing of the clay suspension with the pillaring solution over a time period with heat is the standard method for intercalation of clays. This process can take up to 6 hours to complete as the pillaring solution is added drop-wise and the mixture is stirred for at least 2 hours with heat supplied. Although this method has had success in laboratory synthesis of pillared clays, it is not an ideal preparation technique for large scale production because large amounts of water and heat are necessary.

The use of ultrasonics in this step was reported by Katdare and others (2000). They intercalated a Ca-montmorillonite using ultrasonic treatment over a number of time periods. The most intense and sharpest peaks on XRD patterns were for the calcined sample that had been left in the ultrasonic bath for 20 minutes. They then varied the pillaring solution and determined the optimum Al^{3+} /clay ratio as being 20 meq/g. This PILC (PILCUS) had a basal spacing of 19.2 Å and a BET surface area of 281 m^2/g . To test the thermal and hydrothermal stability of the PILCUS, they heated it to 900°C in 200° steps as well as to 750°C with 100% steam for 8 hours. A similar treatment was given to a PILC (PILCONV) intercalated by the conventional method. The results showed that the structure of PILCONV collapsed at around 700°C while the PILCUS still had some structure at 900°C. The hydrothermal results were the same with the PILCUS still having a basal spacing of 18.1 Å and a surface area of 189 m^2/g . The stability was attributed to the uniform pillaring obtained by the use of ultrasonics. They also reported how the use of ultrasonics did not alter properties such as acidity and catalytic activity.

The same authors, in a later study (Katdare and others 2000), looked at how the exchangeable ions present in the starting clay affected the ultrasonic treatment. They converted the Ca-montmorillonite to Na^+ and La^{3+} forms by ion exchange. This gave exchangeable cations with valencies of +1, +2 and +3. They found that the optimum times for ultrasonic treatment were 5 minutes for the Na form, 20 minutes for the Ca form and 80 minutes for the La form. The increase in time was due to the higher charge ions being more tightly bound to the clay layers. They also concluded that the role of ultrasound is to accelerate the $[\text{Al}_{13}]^{7+}$ diffusion within the clay layers.

This method of intercalation has a number of advantages that help to make large-scale production of pillared clays more viable. First, it reduces the time needed from several hours to less than 30 minutes. It also requires no heat for the process, thus saving in costs and reducing the safety risks, although some safety issues arise with ultrasonics that would need to be addressed. Finally, the clay suspension required can be more concentrated compared to conventional methods, thus using less water and space.

Fetter and others (1996) also looked at a way to speed up the intercalation step by using microwave irradiation. They made up a 10 wt% clay solution and added aluminium chlorohydrate to it making an Al/clay ratio of 5mmol/g. The sample was sealed and subjected to microwave irradiation for various time periods and then pillared by conventional methods. The samples prepared using microwaves gave surface areas some 20-30% higher than samples prepared by the conventional method (ie. mixing for 18 hours). They also found that the irradiation time had little effect on the surface area with a maximum of 347 m²/g being attained after only 5 minutes. In a later study, Fetter and others (1997) were able to similarly prepare a pillared clay using microwave irradiation for 7 minutes but with a more concentrated starting clay slurry of 50 wt%. They achieved a surface area of 331 m²/g, some 87 m²/g higher than the sample they prepared by the conventional method.

Separating and Washing

This step serves to remove any excess ions that are present in preparation for the calcining of the intercalated clay. The separation can be done by filtration or, for a faster result, centrifugation. The washing procedure is more time consuming, as it usually requires the re-suspension of the separated clay in deionised water with stirring for a time period. This process is done a number of times, usually until the filtrate is free of chloride ions as determined by the AgNO₃ test. All of this is time consuming and would be hard to scale-up as vast amounts of water would be required.

Thomas and Occelli (2000) examined the effect that washing had on an Al intercalated montmorillonite. They examined samples of the intercalated clay after

each washing up to 4 times with 400 cm³ of deionised water as well as a sample without any washing. The XRD results showed a broad weak peak for the unwashed sample, which then shifted to 18.9 Å for the first washing, and this reflection became sharper with subsequent washing. They conclude that the initial cations present in the interlayer space were not Keggin ions but that they were formed, "*in situ* by base hydrolysis of the different oligomers present". Hence, the washing procedure is necessary to form stable PILCs as their stability is related to the formation of these Keggin ions.

Aceman and others (2000) examined how allowing the clay to age in the pillaring solution and how the use of dialysis compared to conventional washing methods. They also determined that initially aluminium is adsorbed into the interlayer space either in a monomeric state or as small oligomers. Several days were needed for these species to undergo hydrolytic oligomerization to form Keggin-like ions. This could only occur however, if the excess Al, Na and Cl ions had been removed by washing or by dialysis. For dialysis they put the intercalated sample in a Visking dialysis bag dipped in double-distilled water for one week at room temperature. For laponite and hectorite samples, the dialyzed and non-dialysed samples showed similar poor thermal stability. For montmorillonite, the dialyzed sample was comparable to the sample washed four times. For beidellite and saponite, the dialyzed samples gave the best thermal stability results with XRD peaks being more intense and sharper than those of the washed sample.

Introduction of organic molecules

The use of organic molecules, such as surfactants, in the pillaring solution to act as a swelling has also been examined. This helps to reduce significantly the amount of water required while also making the clay easier to filter. It involves the introduction of an organic molecule into the interlayer along with the pillaring species. The organic molecule, of known shape and size, can later be removed by heat to leave a more regular pore structure. By investigating how such organic molecules affect the pillaring process, specific pore sizes can be designed.

Michot and Pinnavaia (1992) incorporated a nonionic surfactant of general formula $C_{12-14}H_{25-29}O(CH_2CH_2O)_5$ with the usual Al-pillaring solution. The resultant PILC had a more uniform micropore distribution and a sharper, more symmetrical 001 reflection compared to one prepared without surfactant. The basal spacing was however smaller than normal (15.3 Å) but this was attributed to the surfactant limiting the condensation of Al_{13} units within the interlayer space. The surface area (305 m²/g) was also slightly larger than the conventional PILC (279 m²/g) and contained more mesopores. An important feature of this method is that the intercalated product is easily filtered and could be washed free of excess ions using two thirds less water than that required by the conventional method.

Galarneau and others (1995) converted a Li-fluorohectorite to a quaternary-ammonium exchanged form and then mixed with a solution of neutral amine and tetraethylorthosilicate (TEOS). The interlayer space was swollen which allowed the TEOS to enter and hydrolyse. The surfactants were then removed by calcining at 600°C leaving a rigid silica framework between the layers. The basal spacings of the PILC ranged from 14.9 to 23.4 Å, depending on the chain length of the neutral amine used.

Suzuki and others (1988) were able to use polyvinyl alcohol as a pre-swelling agent for pillaring of montmorillonite with Al_{13} . Hectorite was similarly (Suzuki and others 1991) and they showed how the presence of polyvinyl alcohol provided favourable conditions to allow smaller Al cations to hydrolyse into larger ones. As they increased the concentration of aluminium chlorohydroxide in the pillaring solution, the basal spacings increased, as did the pillar concentration. This was not the case with the PILC prepared without polyvinyl alcohol.

Cracking of vegetable oil

As mentioned earlier, transesterification of vegetable oil is currently the method of choice for conversion to a useable fuel. Many studies have however been done on the upgrading of such oils using various catalysts and reaction conditions. These studies have examined the products obtained by the cracking processes and have tried to correlate the effect that these variables have on the final products. The problem with

any research done in this field is that because the starting material (vegetable oil) is a complex mixture that changes drastically between types, it is difficult to extrapolate or replicate the results. Hence, the reporting of any results in this review must be used as a guide only and can not be expected to extend totally to the anticipated outcome of this project.

Canola oil

Katikaneni and others (1995a) used a number of catalysts, including Al- PILC, to convert canola oil to fuel using a fixed bed reactor. They examined how each catalyst performed with respect to organic liquid product (OLP) yield, selectivity and coke formation. They found that HZSM-5 gave the highest yield of OLP of 63 mass % with the pillared clay being third giving a 55 mass % yield. The OLP of the PILC contained more aliphatic hydrocarbons than the other catalysts and the least amount of aromatic hydrocarbons. Their results showed that as the pore size of the catalyst was increased, the conversion of canola oil, the coke formation and the selectivity for aliphatics increased while the yield of hydrocarbons and the selectivity for aromatics decreased. This led them to the conclusion that medium pore catalysts enhanced the initial cracking and deoxygenation reactions needed for an optimum fuel yield. They were also able to propose a reaction pathway for conversion by looking at the products formed (Fig. 4). After the initial cracking occurs (step 1) further reaction steps were proposed for the heavy hydrocarbons and oxygenates formed. Both are thought to undergo secondary cracking (steps 2 and 5) to form gas products. The heavy oxygenates can also be deoxygenated (step 4) to form CO, CO₂, methanol and acetone while the heavy hydrocarbons undergo aromatization (step 3) to form C₉+ aromatic hydrocarbons. The authors suggest that the initial cracking occurs in the inter-planar space and then diffuses into the pores of the clay sheets where further reactions proceed. One of these reactions is polymerization, which leads to coke formation and a clogging of the inter-planar space.

A further study by these authors (Katikaneni and others 1995b) showed how co-feeding with steam during the reaction helps to increase olefin formation as well as increase the catalyst life by decreasing coke formation.

Vonghia and others (1995) suggested that the initial cracking reaction occurred via two mechanisms: β -elimination and γ -hydrogen transfer (Fig. 5). Both are initiated by the bonding of a carbonyl oxygen to a Lewis acid site on the catalyst. It is possible for both reactions to occur on a triacylglyceride molecule but β -elimination can only happen once.

The effect that acidity, basicity and shape selectivity of a catalyst had on the conversion of canola oil was examined by Idem and others (1997). The various catalysts and their properties are listed in table 3. An empty reactor run was performed to evaluate the contribution of each catalyst, and the products of this run led them to the conclusion that initial decomposition of the oil to heavy hydrocarbons and heavy oxygenates was independent of catalyst properties.

The effect shape selectivity had on the product was evaluated by comparing HZSM-5 and silicalite against the empty reactor run. These catalysts gave a higher OLP yield along with a lower gas yield. This led them to the conclusion that only limited secondary cracking was allowed because of the long molecules diffusing through the pore structure with minimal C-C bond scission. The OLP from the two catalytic runs had a higher fraction of C₇-C₉ aromatic hydrocarbons. This was attributed to an increase in cyclization and aromatisation reactions (eg. Diels-Alder and dehydrogenation) that are allowed to occur within the pores of the catalyst.

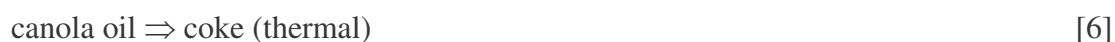
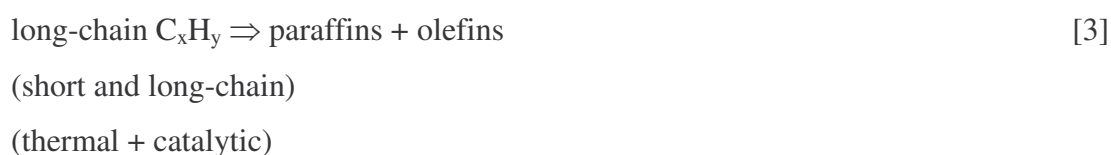
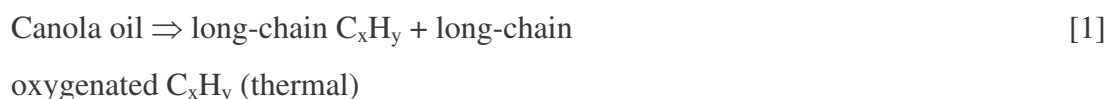
HZSM-5, silica-alumina and γ -alumina were compared to evaluate the role of catalyst acidity in conversion products. Product distribution for runs using silica-alumina and γ -alumina were very similar to the empty reactor run with yields being slightly higher. As both of these catalysts contain Brønsted and Lewis acid sites, it was suggested that the acidity of the catalyst did not determine the product selectivity.

The increase in OLP yield and total aromatic hydrocarbons obtained by using HZSM-5 was attributed mainly to its shape selective properties, not acidity.

To examine how basicity affected the product yield, they used calcium oxide and magnesium oxide as catalysts. The results showed that the presence of basic centres inhibited secondary cracking and produced large amounts of residual oil.

Katinkaneni and others (1998), in a later study, looked at the conversion products using HZSM, HS-mix and silica-alumina catalysts but they carried out the reactions

in a fluidised bed reactor. This involved the continuous flow of argon through the catalyst bed, which assists in catalyst regeneration. They summarized the reaction sequence (below) proposed from previous studies and related the catalyst properties to the conversion products by means of this sequence.



The Brönsted acidity of the catalyst can enhance the reactions that occur in steps 2-4 and this was confirmed by their results which showed that canola oil conversion increased as the reaction temperature and catalyst acid site density was increased. Such conversions were also enhanced by a decrease in fluidising gas velocity, as there was a greater contact time with the catalyst. The selectivity for OLP in a fluidised bed reactor was lower than that achieved in a fixed bed reactor. This too was

related to the shorter contact time in the fluidised-bed reactor, which did not allow the formation of additional OLP from C₂-C₅ olefins in steps 4 and 5.

Palm oil

Leng and others (1999) used a fixed bed reactor to crack palm oil over HZSM-5 catalyst. The maximum formation of gasoline range hydrocarbons was achieved at 400°C with a low space velocity. The conversion of palm oil was low (40-70%) compared to those using canola oil (Idem and others 1997) where conversions up to 100% were achieved. This was attributed to the fact that palm oil contains more saturated fatty acids (palmitic acids) than canola oil and these have a greater stability than unsaturated fatty acids. A similar reaction pathway (Fig. 6) to that shown for canola oil was proposed for palm oil conversion over HZSM-5, with deoxygenation and primary cracking being the initial reactions. Likewise, secondary reactions were controlled by catalyst properties (eg. acidity and pore structure) as well as the reaction conditions (eg. temperature and flow rate).

Twaiq and others (1999) also looked at palm oil conversion using HZSM-5 as well as zeolite β and ultrastable Y (USY) zeolites. They were able to achieve conversions of up to 99 wt % with gasoline yields of 28 wt%. They concluded that HZSM-5 was the best catalyst for conversion, gasoline yield, selectivity for aromatic and lower coke formation.

Sunflower oil

A study by Dandik and others (1998) examined the products of the conversion of used sunflower oil with HZSM-5 using a special fractionating pyrolysis reactor. A conversion of 96.6% was achieved at 420°C with an OLP yield of 33%. The length of the fractionating column on the reactor had an effect on the OLP content with an increase in length giving a significant increase in n-alkene content. This is given as a variable that can be adjusted to optimise the fuel product.

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Table 1 - Basal spacings, (\AA) at different temperatures (González and others 1992)

Temperature\ Sample	Al-PILC-I	Al-PILC-II	AlGa-PILC
25°C	19.0	18.2	19.2
300°C	18.0	18.2	19.0
500°C	17.2	17.3	17.7
700°C	–	–	17.3

Table 2- Properties of SiAl PILCs produced by 2 methods (Sterte and Shabtai 1987)

Method of preparation	Si/Al ratio in hydroxy-SiAl solutions	Surface area (m ² /g)	d(001)(Å)
1	0.0	458	19.2
1	0.53	369	19.3
1	1.04	324	19.5
1	2.18	278	19.0
2	0.0	499	17.6
2	0.5	498	17.7
2	1.0	460	17.2
2	2.0	343	17.0

Table 3- Characteristics of catalysts used by Idem and others (1997).

Catalyst type	Acidic, basic or neutral	Type of acidity	Si/Al ratio	Strength of acid or basic sites	Pore structure	Pore size (nm)	Surface area (m ² g ⁻¹)	Shape selectivity
HZSM-5	Acidic	Mostly B	56	Strong	Crystalline	0.54	329	V. high
Silicalite	Neutral	None	No Al	N/A	Crystalline	0.54	401	V. high
Silica	Neutral	None	No Al	N/A	Amorphous	11.46	211	None
γ-alumina	Acidic	B and L	0	Moderate	Amorphous	14.93	241	None
Silica-alumina	Acidic	B and L	0.79	Moderate	Amorphous	3.15	321	None
Calcium oxide	Basic	None	N/A	Strong	Amorphous	11.86	7	None
Magnesium oxide	Basic	None	N/A	Weak	Amorphous	15.22	27	None
Empty reactor	neutral	none	N/A	N/A	N/A	N/A	None	None

Figure captions

Fig. 1 Compositions of the most common vegetable oils.

Fig. 2 Schematic representation of the repillaring process

Fig. 3 Schematic model of the SiAl pillaring complex (modified after Sterte and Shabtai, 1987)

Fig. 4 Reaction pathway for canola oil conversion using pillared clay catalysts as proposed by Katikaneni and others (1995a,b).

Fig. 5 Two possible pathways for cracking reactions via β -elimination and γ -hydrogen transfer.

Fig. 6 Proposed reaction pathway for cracking of palm oil over HZSM-5 (Leng and others 1999).

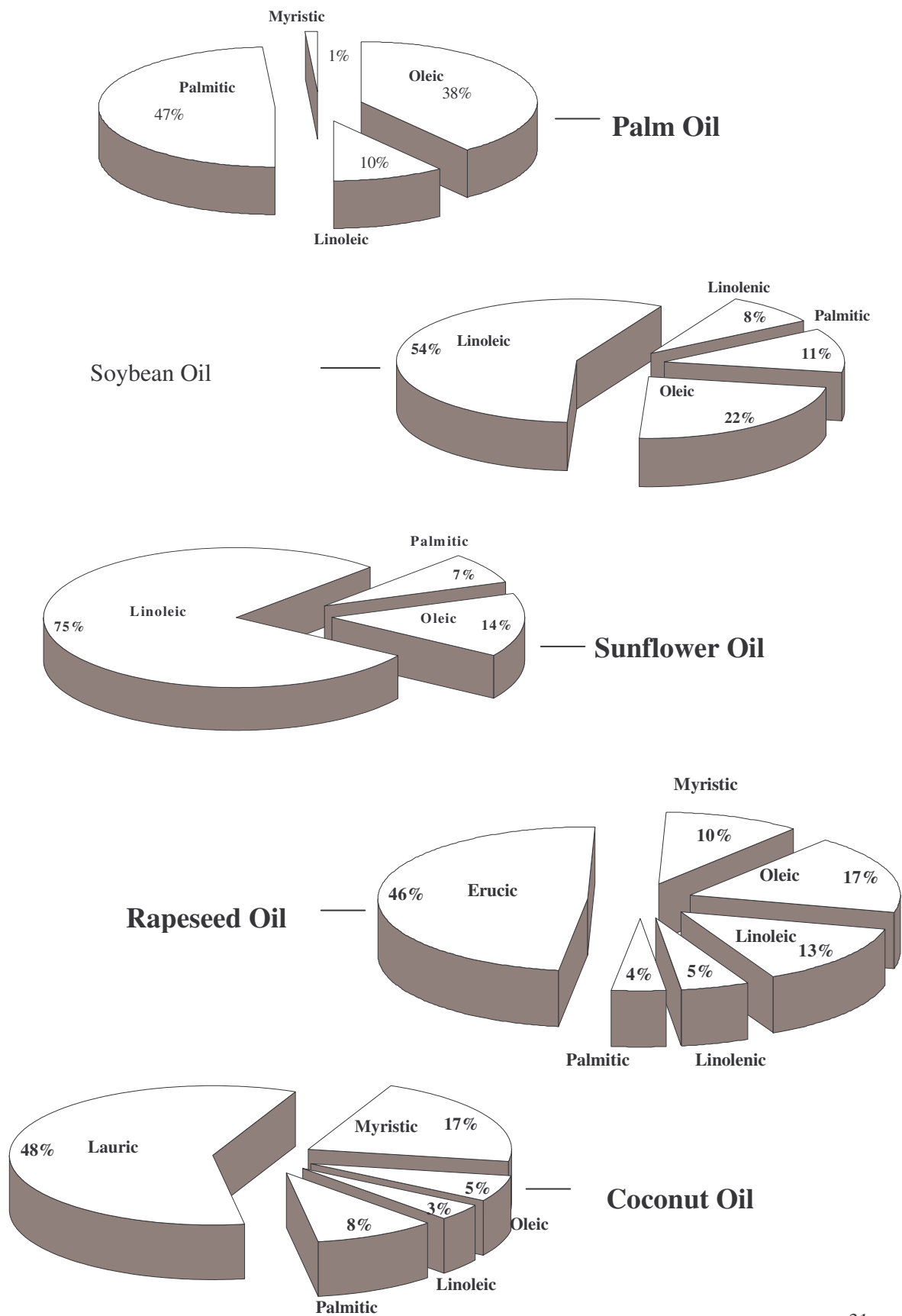
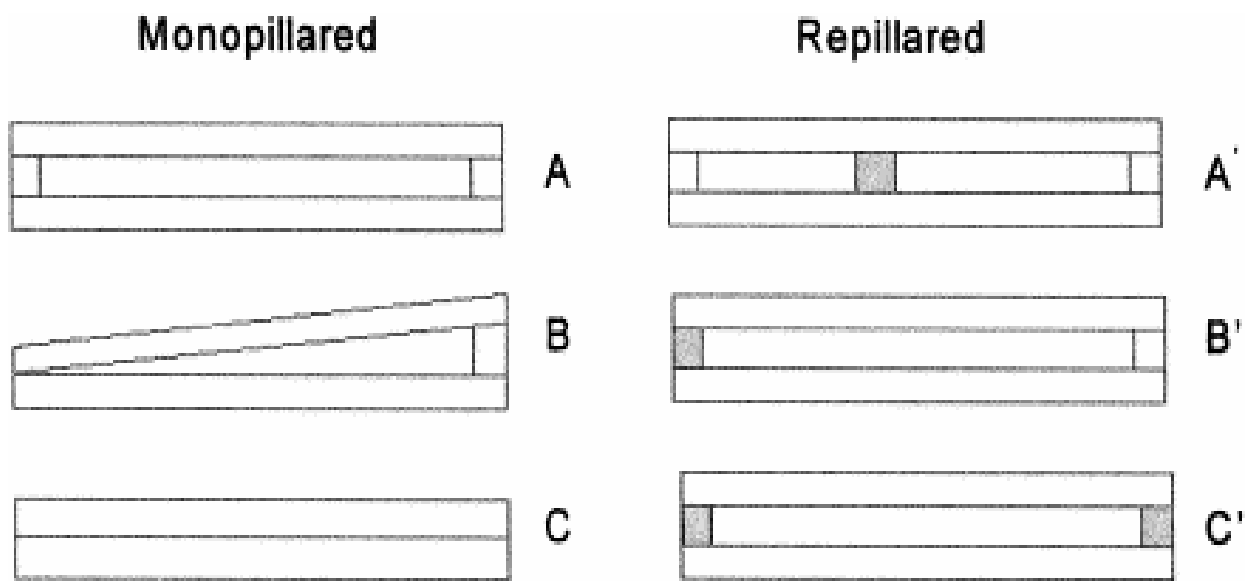


Fig. 1

Fig. 2



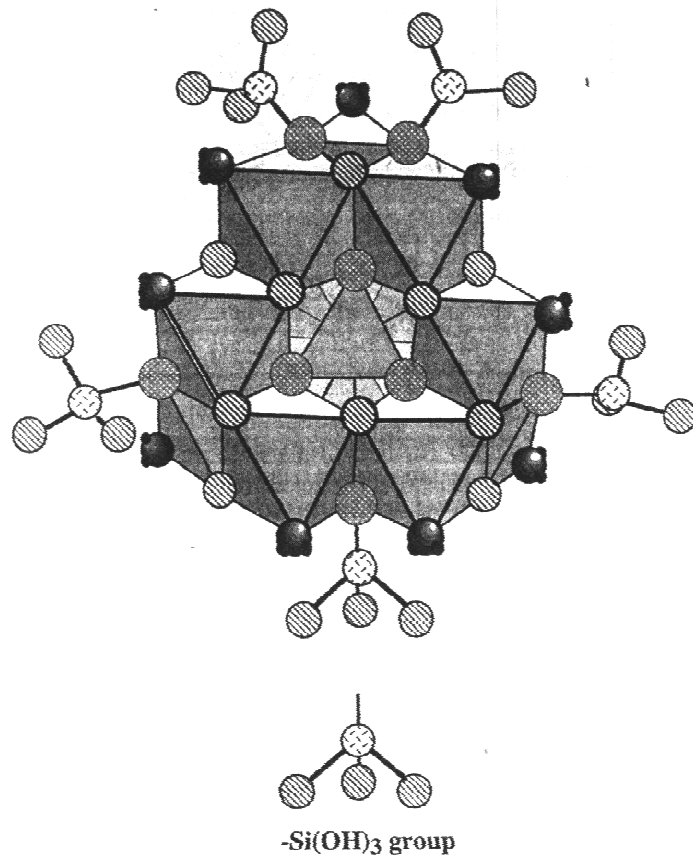


Fig 3

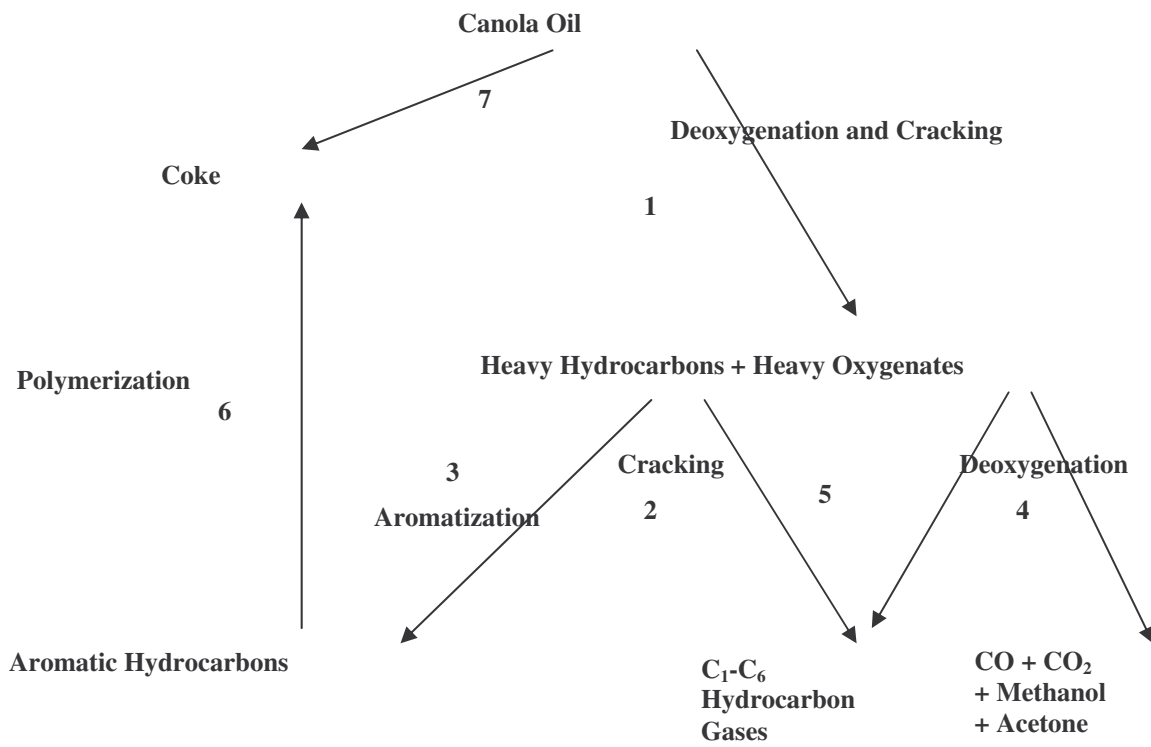
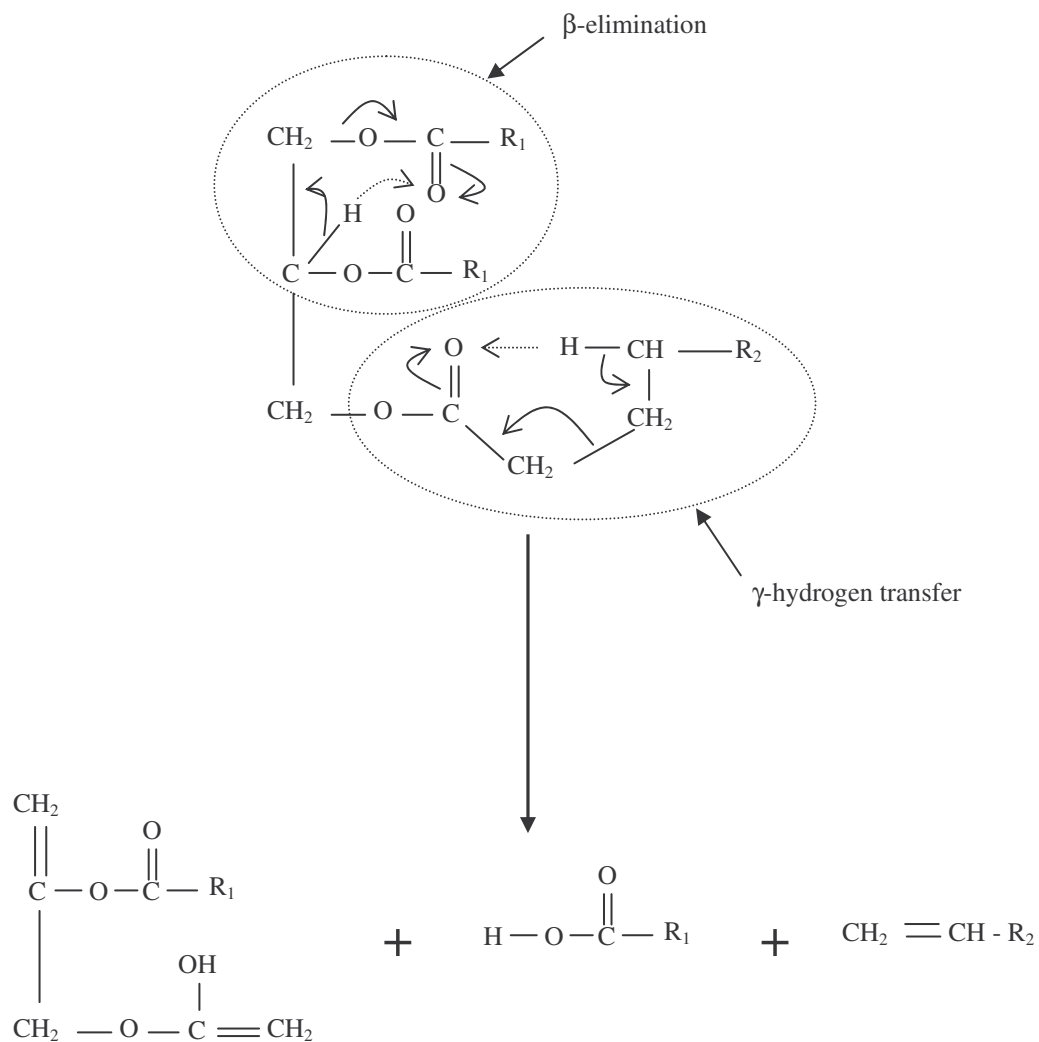


Fig. 4

Fig. 5



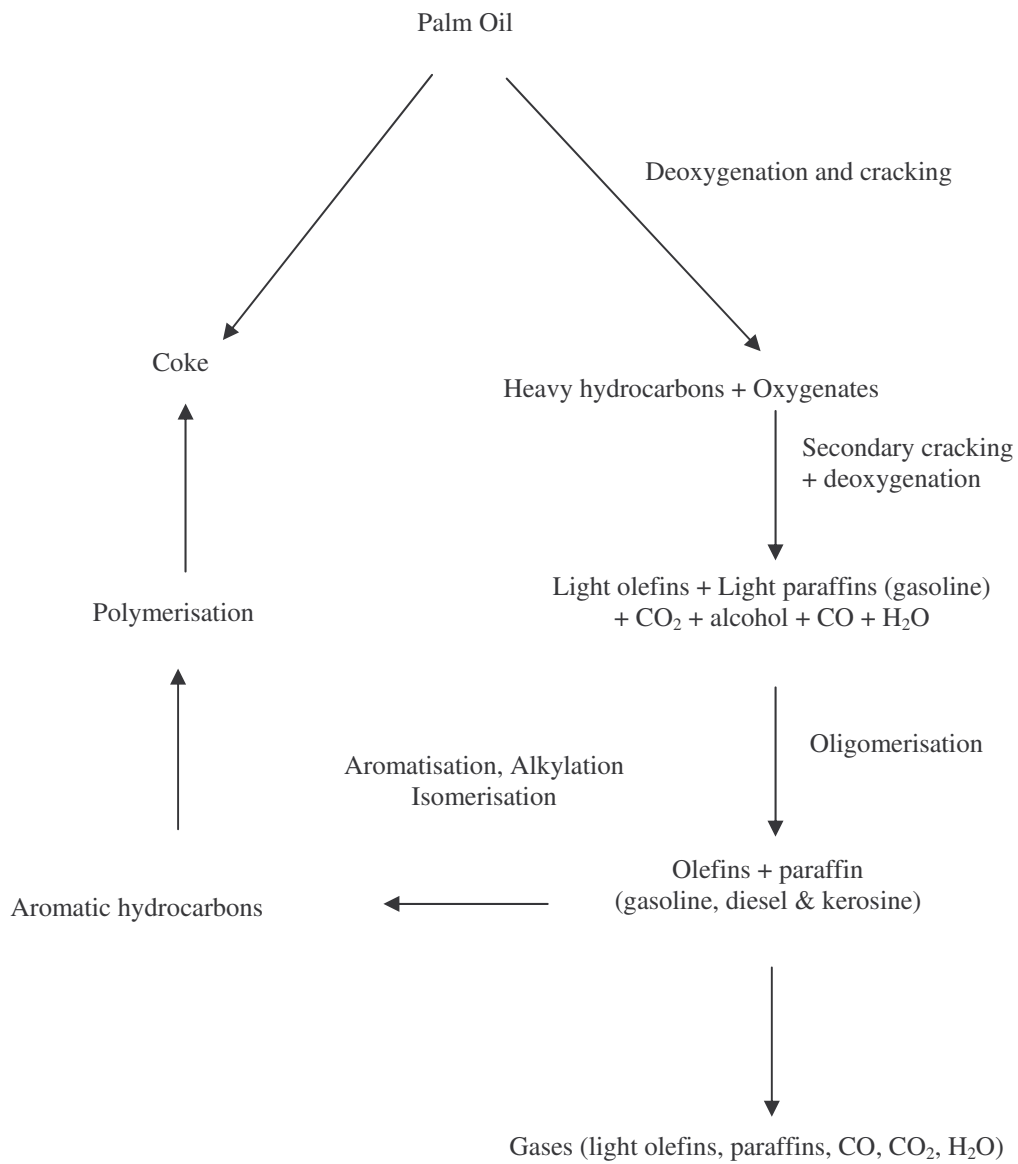


Fig. 6