MAKING AN ECO FRIENDLY BOARD BY USING LIGNIN- SOY BASED NATURAL ADHESIVE

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**A thesis submitted in fulfillment
of the requirements for the award of degree of
Bachelor of Chemical Engineering**

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JANUARY 2012

ABSTRACT

The wood composite industry in Malaysia comprises of 12 MDF and 10 particleboard plants with an installed capacity of about 5 million tons per year. The total production capacity is approx 2.5 million cubic ton. Most of the MDF boards are exported to US, Europe and Asian market. At present formaldehyde based adhesive such as urea formaldehyde (UF) and phenol formaldehyde (PF) is used as the binder. The main problem with these adhesives is continuous emission of formaldehyde vapors that are carcinogenic in nature. A number of developed countries have put ban on the import of these boards. The objective of this research is to modify the lignin content of wood fibers by using soy flour which is available in Malaysia. This modified lignin based adhesive is expected to replace the use of artificial resins like UF and PF and because of commonly available soy flour it will be economical and eco friendly. The fiberboards were prepared from three different adhesives, which are urea formaldehyde (UF) resins, natural adhesive (lignin) and protein-lignin based adhesives. Hot pressing at constant temperature 180ºC and pressure 2MPa within 4 minutes pressing was done to form the boards. For each board were tested for mechanical properties including modulus of rupture (MOR), thickness swelling (TS) and internal bond strength (IB). Results showed that SF, lignin, acetic acid (CH_3COOH) and sodium hydroxide were all essential components for the adhesive and the SF: lignin: CH_3COOH weight ratio of 3: 75: 10 with pH 11 resulted in the highest value of MOR, IB strength and water resistance. Fiberboard made from lignin- soy based natural adhesive shows promise and possibilities for industrial application in wood composite industries. Moreover, lignin- soy based adhesive used resulting in boards with good mechanical properties without toxic effect to humans.

ABSTRAK

Industri kayu komposit di Malaysia terdiri daripada 12 loji MDF dan 10 loji partikel dengan keupayaan mengisi kira- kira 5 juta tan setahun. Jumlah kapasiti pengeluaran kira- kira 2.5 juta tan padu. Kebanyakan papan MDF dieksport ke Amerika Syarikat, Eropah dan pasaran Asia. Masa kini, pelekat berasakan formaldehid seperti Urea Formaldehid (UF) dan Fenol Formaldehid (PF) digunakan sebagai pengikat. Masalah utama dengan pelekat- pelekat ini dengan pelepasan wap formaldehid secara berterusan yang bersifat karsinogen pada alam semulajadi. Beberapa negara maju telah mengharamkan untuk mengimport papan ini. Objektif kajian ini adalah untuk mengubah suai kandungan lignin gentian kayu dengan menggunakan tepung kacang soya yang terdapat di Malaysia untuk dijadikan pelekat semasa proses penghasilan papan. Pelekat yang berasakan lignin yang telah diubah suai ini dijangka dapat menggantikan penggunaan resin tiruan seperti UF dan PF dan kerana tepung soya biasanya mudah didapati, menjimatkan dan mesra alam. Papan fiber telah disediakan daripada tiga pelekat berbeza yang terdiri daripada resin UF, pelekat asli (lignin) dan pelekat berasaskan lignin- soya. Pemanasan pada suhu tetap sebanyak 180°C dan tekanan 2MPa selama 4 minit untuk menekan serbuk kayu untuk membentuk papan fiber. Bagi setiap papan fiber yang terhasil hendaklah diuji sifat- sifat mekanikalnya termasuklah MOR, IB dan TS. Keputusan menunjukkan bahawa larutan pelekat yang terdiri daripada komponen tepung soya, lignin, CH_3COOH dan NaOH dengan nisbah berat tepung soya: lignin: CH_3COOH sebanyak 3: 75: 10 dengan pH 11 menghasilkan nilai tertinggi untuk MOR dan IB selain mempunyai ketahanan air paling tinggi. Papan yang dibuat daripada pelekat berasakan lignin- soya menunjukkan hasil yang memberangsangkan dan ada kemungkinan untuk bersaing dalam industry komposit kayu. Tambahan pula, pelekat berasakan lignin- soya yang digunakan pada papan mempunyai ketahanan yang tinggi tanpa kesan toksik kepada manusia.

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CARB	-	California Air Resources Board
CH_3COOH	-	Acetic Acid
DEO	-	1, 2, 7, 8-diepoxyoctane
HDF	-	High Density Fiberboard
HNO_3	-	Nitric Acid
GA	-	Glutaraldehyde
IB	-	Internal Bonding
LDF	-	Low Density Fiberboard
LiP	-	Lignin Peroxidase
LVL	-	Laminated Veneer Lumber
MA	-	Maleic Anhydride
MAP	-	Marine Adhesive Protein
MDF	-	Medium Density Fiberboard
MnP	-	Manganese Peroxidase
MOR	-	Modulus of Rupture
MUF	-	Melamin- Urea- Formaldehyde
NaOH	-	Sodium hydroxide
OSB	-	Oriented Strand Board
PAE	-	Polyamidoamine-Epichlorohydrin
PEI	-	Polyethylenimine
PF	-	Phenol- Formaldehyde
pMDI	-	Polymeric 4, 4’-diphenylmethane diisocyanate
PVA	-	Polyvinyl Acetate
SF	-	Soy Flour
SPC	-	Soy Protein Concentrate
SPI	-	Soy Protein Isolate
UV	-	Ultraviolet
WPC	-	Wood- Plastic Composites

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Lignin comprises as much as 40 percent of wood's mass, therefore the development and modification for the use of lignin is an attractive and environmentally intelligent goal. Lignin's random and non- crystalline network structure makes it a very thermodynamically stable biopolymer (Glasser, 1981).

Wood composites are a class of materials that generally consist of solid fragments of wood that are reconstituted in a form fit for a designated end- use by some sort of adhesion process. Fiberboards, plywood, particleboard, oriented strand board (OSB) and wood plastic composites are all members of this class of composites (J. Youngquist, 1999). Over time, wood composites have been reconstituted from ever- smaller wood fragments, progressing from plies to strands to fibers to fine 'flour' measuring only microns in size. Wood composites are capturing ever larger markets, partially in response to reduction in the supply of solid, large dimension timber (S. Shook, I. Eastin, 2001). Composites in general are materials that combine the high strength and stiffness characteristics of a fiber (or particle) with the ductility of a (continuous) matrix (J.E. Gordon, G. Jeronimidis, 1980). In many man- made composites the fiber matrix interface is the weakest point resulting in 'fiber pull- out' and failure before the fiber reaches its true strength potential (B. Harris, 1980). Many wood composites also suffer from the high density that is the result of thermal processing under high pressure conditions (A. R. Sanadi, D.F. Caulfield, R.E. Jacobson, 1997). The ideal wood-like composite would combine the features of a high strength and high stiffness (hollow) fiber embedded in a continuous matrix from which it never (under any condition of moisture or temperature) separates inter- facially, and with which it produces a lightweight material (G.M. Bond *et al.*, 1995).

Bonding of lignocelluloses material is essential for the manufacture of particleboard, fiberboard, OSB, laminated wood products and plywood. Bonding of wood fibers or particles can be achieved by high pressure and temperatures, a phenomenon known as auto- adhesion. The effect can be used for making binderless boards and panels, but compared to boards made with synthetic adhesives the mechanical properties are inferior.

Bonding of wood fibers and particles by adhesives can be accomplished by forming a resinous matrix in which the particles or fibers are bonded together, e.g. by mechanical entanglement or covalent cross- linking (Claus Felby *et al.*, 2002).

In current commercial bonding process, an adhesive is spread or sprayed on the surface of the material. Procedures have been proposed to create adhesion through formation of wood- to- wood chemical bonds, but have not met commercial acceptance (D. Yelle *et al.*, 2004).

Wood adhesives are potentially a huge market for the oversupplied soybean. As a matter of fact, soy-based adhesive was widely used in the commercial production of plywood in the 1930s-1960s. Soy-based wood adhesives have many advantages such as low cost, easy handling, low pressing temperature (Li K. *et al.*, 2004). However, they also have many inferior properties such as low strength and water-resistance of the resulting wood composite panels. Because of their inferior properties, they have been virtually replaced by formaldehyde-based adhesives since the 1960s. However, soybean represents an ideal raw material for making wood adhesives because it is abundant, renewable, environmentally friendly, and readily available.

There has been a renewed interest in development of soy-based wood adhesives in recent years. Various new methods have been investigated for improving the strength and water-resistance of wood composite panels bonded with soy-based adhesives. It was demonstrated that the treatment of soybean protein with alkali and protease enzymes significantly improved the strength and water-resistance of plywood samples bonded with the modified soy proteins (Hettiarachchy et al., 1998,. Hettiarachchy *et al*., 1995, Kumar R. *et al*., 2004)

Regarding wood products made with the increasingly expensive petroleum-derived adhesives, manufactures of medium- density fiberboard (MDF) and particle board (PB); structural panels such as plywood and oriented strand board (OSB); solid- wood joints, are keen to reduce production costs and harmful formaldehyde emissions from the adhesives and to improve product recyclability.

In addition, the adhesive components are derived from petroleum, which is increasingly more expensive (Sellers T., 2001, Maloney TM., 1996) in North America alone, the total amount of wood adhesive solids used for wood composites was around 1.8 MT (Sellers T., 2001). Therefore, meeting these challenges calls for innovative approaches to minimize the amount of binder, e.g. masonite boards, while ensuring product quality. Another important topic related to wood products is the chemical modification of their surface and bulk properties to improve their durability, enhance their properties strength, range of application and compatibility with other materials for use in hybrid products such as wood- plastic composites. The cost of pulping may also be an issue for wood products such as fiberboards whose manufacturing process includes pulping.

In search for solutions to the above- discussed challenges, the goal of this research is to use soy flour to modify lignin as an adhesive of wood fibers before make it into composite boards such as MDF and as a means for making boards without petroleum- derived wood adhesives and to promote more environmental friendly, less expensive alternative for bonding of wood in the wood composite industry.

1.2 Problem Statement

Wood composite boards such as MDF and PB such as chipboard are commonly used for interior building and furnishing (Sellers T., 2001, Maloney TM., 1996, Youngquist JA., 1999). The thermosetting adhesives used in MDF and PB, mainly UF but also known as melamin- urea- formaldehyde (MUF) and phenol-formaldehyde (PF), account for 10% of the board mass.

Many grades of high- density fiberboards (HDF boards, hardboards) also require a certain amount of binder. Formaldehyde is used in glues in composite wood products such as medium density fiberboard or MDF and particleboard which are generally recognized as being the highest formaldehyde- emitting composite wood product (used for kitchen and bathroom cupboards and drawers, and wardrobes); particleboard (used as sub- flooring and shelving and in cabinetry and furniture); and plywood paneling (used for decorative wall covering and used in cabinets and furniture).

Occupational exposure to formaldehyde by inhalation is mainly from three types of sources: thermal or chemical decomposition of formaldehyde- based resins, formaldehyde emission from aqueous solutions (for example, embalming fluids) and the production of formaldehyde resulting from the combustion of a variety of organic compounds (for example, exhaust gases).

Formaldehyde has been re-classified as a human carcinogen by International Agency for Research on Cancer (International Agency for Research on Cancer, 2004). It is well established that formaldehyde is released in the production and use of wood composites bonded with these formaldehyde-based adhesives, especially UF. The California Air Resources Board (CARB) estimates that as much as 400 tons of formaldehyde is emitted by the products bonded with UF each year in California (Composite Wood Products Fact Sheet, 2006). The emission of formaldehyde mainly comes from residual free formaldehyde in adhesives and the hydrolytic product of the adhesives. Cured UF resins are susceptible to hydrolysis in the presence of water or moisture to release formaldehyde. Acidic environment and elevated temperatures can speed up the hydrolysis. Cured PF resins are more resistant to hydrolysis than cured UF resins. Thus, residual free formaldehyde is mainly responsible for the formaldehyde emission from PF resins and PF-bonded wood composite panels.

Formaldehyde can be toxic, allergenic and carcinogenic. In addition, the health hazards of formaldehyde (carcinogenic to humans) emissions during board production and end- use of fiberboard products made with amino resins (UF or MUF) are a concern among consumers and manufacturers (Sellers T., 2001, Youngquist JA., 1999). Because formaldehyde resins are used in many construction materials it is one of the more common indoor air pollutants. At concentrations above 0.1 ppm in air formaldehyde can irritate the eyes and mucous membranes, resulting in watery eyes. Formaldehyde inhaled at this concentration may cause headaches, a burning sensation in the throat and difficulty breathing, as well as triggering or aggravating asthma symptoms. Formaldehyde has also been shown to have short- term health effects, including burning sensations in the eyes and throat, nausea and difficulty in breathing.

Formaldehyde is also the primary cause of methanol’s toxicity, since methanol is metabolized into toxic formaldehyde by alcohol dehydrogenase. Formaldehyde is converted to formic acid in the body. Emission of harmful formaldehyde from adhesive is spread widely, exposure to its toxicity and volatility will course major problem and will be resulting in the health diseases of human.

The non-renewable nature of the raw materials for making currently used formaldehyde-based adhesives and the hazardous issues associated with formaldehyde emission have generated a need for the development of a formaldehyde-free wood adhesive from renewable materials.

1.3 Objectives

The research was conducted to achieve the following objectives:

1) To improve the polymerization behavior of lignin content of wood fibers by adding soy flour to make natural adhesive.
2) To study the lignin-soy based adhesive and its broad scope that can gives promise and possibilities for industrial growth worldwide.

1.4 Scopes of Study

In order to achieve the objectives, the following scopes have been identified:

1) Reviewed on the literature review on the latest development and related study on lignin modification in wood fiber.
2) A pre-treatment of the fibers with the soy flour adhesive followed by hot pressing to made boards.
3) Tested the mechanical properties of boards.
4) Analyzed data

1.5 Research Contributions

Modifications of lignin content in the woods using soy flour treatment are beneficial to the environment and society. There are several benefits which are:

1) Contribute to the personnel protection in preventing the harmful emission substances from adhesives which is reduces health hazards for production personnel.

2) Promote a more environmental friendly and less expensive alternative for bonding of wood in the wood composite industry which is preserving and protecting environment.

Both economical and health benefits could thus be obtained from binderless (synthetic resin- free) production processes. Moreover, the 'mega trends' of favoring renewable raw materials and waste elimination are compatible with binderless composite boards (Sellers T., 2001).

CHAPTER 2

LITERATURE REVIEW

2.1 Wood Composites

Wood composites are made from woody materials in various forms such as veneer and particles, and some non-wood materials such as an adhesive. Compared to solid wood, wood composites can provide better mechanical and chemical properties such as higher shear strength, and improved resistance to fire, weathering and biological degradation. Wood composites can be made with various sizes and shapes that are not easily obtainable from logs. In addition, waste materials from saw mills such as chips, sawdust, and shavings can be fully utilized in the production of wood composites. Wood composites can have more uniform properties at different directions than solid wood.

Wood composites can be classified into two categories: traditional wood composites including wood- based panels and engineered lumber, and advanced hybrid composites such as wood- plastic composites (WPC) and inorganic- bonded composites. The current wood composites market is mostly occupied by traditional wood composites such as medium density fiberboard (MDF), plywood, oriented strand board (OSB) and particleboard.

2.1.1 Medium Density Fiberboard (MDF)

Fiberboard is a wood composite panel made with wood fibers, an adhesive and some additives such as wax. Fiberboard is typically classified according to its density: low density fiberboard (LDF), MDF and high density fiberboard (HDF). The densities of these fiberboards are 150-450 kg/m^3 for LDF, 600-800 kg/m^3 for MDF, and 850-1100 kg/m^3 for HDF [4]. MDF has a higher strength, and a higher moisture resistance than particleboard.

MDF is widely used for furniture and flooring. It is also used for making interior door skins, moldings and interior trim components.

MDF is predominately made with UF resins. However, UF-bonded MDF has a low water-resistance and emits formaldehyde, which has generated a need for replacement of UF resins in making MDF (Callum D.M., 1999).

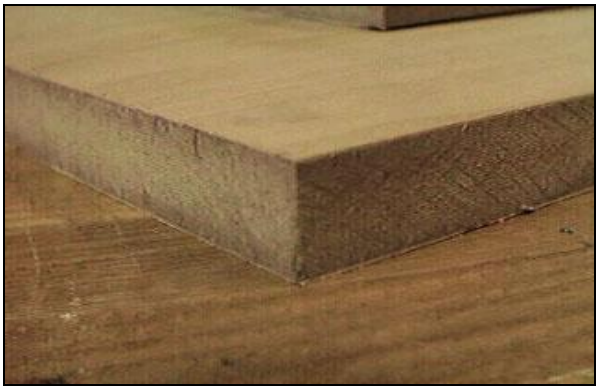

Figure 2.1: Medium Density Fibreboard

2.1.2 Plywood

Plywood is composed of veneers bonded with an adhesive under heat and pressure. Wood grains in adjacent layers are typically perpendicular to each other, which imparts plywood panels' relatively uniform properties in all directions.

Plywood typically has an odd number of layers. Plywood is widely used for making houses, kitchen cabinets, and furniture.

There are two types of plywood: structural softwood plywood and decorative hardwood plywood. Softwood plywood is mainly used for exterior structural applications, and hardwood plywood is generally employed for interior applications. The consumption of softwood plywood has been decreasing in recent years (Forest Products Annual Market Review 2000- 2001). However, the demand of hardwood plywood will remain strong for many years to come.

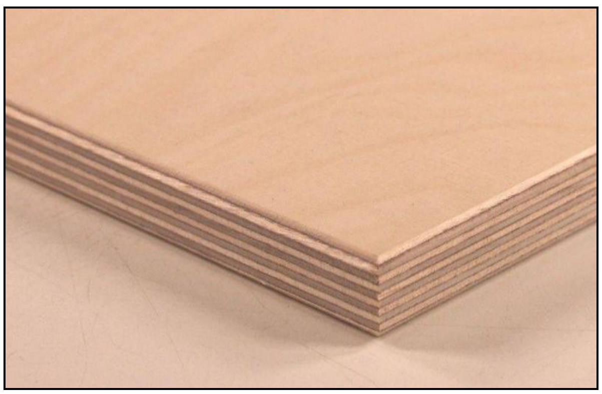

Figure 2.2: Plywood

2.1.3 Oriented Strand Board (OSB)

OSB is a structurally used panel made from adhesives and strands under heat and pressure. Strands at adjacent layers are oriented perpendicularly to each other. OSB can be made from small diameter logs and low quality wood, thus being more efficient in the use of woody materials than plywood. OSB also costs less than plywood, but has comparable strength and stiffness to plywood. Therefore, OSB has rapidly been gaining its market share at the expense of softwood plywood since the mid 1980s although OSB has a shorter history than plywood.

OSB can be used for making I-joints, wall sheathing, sub floors, floor underlayment and many other products.

Different adhesives are typically used for making the face layers and the core layer of OSB. PF resins are typically used for making the face layers, and isocyanates are typically used for making the core. Wax is usually employed in the manufacture of OSB for enhancing the moisture resistance and the dimensional stability of OSB (Wood as an Engineering Material).

Figure 2.3: Oriented Strand Board

2.1.4 Particleboard

Particleboard is a panel product manufactured from small wood particles and an adhesive. The raw materials of particleboard are sawdust, planner shavings, or other relatively homogeneous waste materials from wood industry. Particleboard typically has two face layers made with fine wood furnish and one core layer made with coarse wood furnish. Particleboard is less expensive than solid wood. However, particleboard has a lower dimensional stability in the presence of moisture or water than solid wood. Particleboard is mainly used for making furniture and kitchen cabinets.

UF resins are the most commonly used adhesive for making particleboard. PF, melamine-urea-formaldehyde (MUF) and isocyanates are sometimes used (Wood as an Engineering Material).

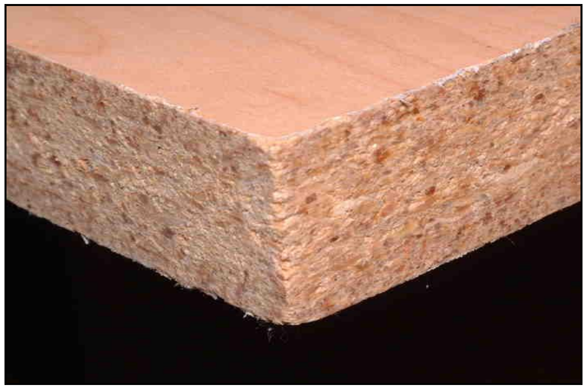

Figure 2.4: Particleboard

2.2 Wood Adhesives

Adhesives are an indispensable component in traditional wood composites. They can significantly affect the physical, mechanical and chemical properties of wood composites. Wood adhesives can be roughly classified into two categories: adhesives from natural materials and adhesives from petrochemicals.

2.2.1 Adhesive from Natural Materials

2.2.1.1 Animal Glues

Animal glues are made from the hide and bones of animals such as cattle, sheep, and fish. They are, in fact, hydrolysis products of collagen, i.e., protein-based adhesives. The protein in the animal glues contains a high amount of an amide group (-CONH-), free amino groups (-NH- ,$-NH_2$) and a carboxylic acid group (-COOH). These functional groups interact with each other within and between protein chains. In addition, these functional groups also interact with wood (Blomquiest R.F. *et al*., 1981). These interactions provide the strength of animal glues and the adhesion. Proteins in different animal glues have different structures and contain different amounts of these functional groups. Therefore, the properties of different animal glues vary significantly.

Animal glues are sold as solid or liquid. The solid animal glues have to be mixed with water before use. Animal glues were once widely used in furniture. However, they have been replaced by synthetic polyvinyl acetate because of their many undesirable properties such as low moisture resistance, susceptibility to biological degradation, and a relatively high price (Eckelman C.A., 1997).

2.2.1.2 Casein- based Adhesive

Casein is a milk protein. Casein protein precipitates when milk is treated with acid. Separation and subsequent drying of the precipitate generate casein (Skeist I., 1990). Casein has high amounts of carboxylic acid groups and can readily dissolve in an alkaline medium such as lime solution or sodium hydroxide solution. The carboxylic acid groups in casein can react with divalent or polyvalent metal ions to form crosslinked networks. The treatment of casein with the metal ions improves the water-resistance of the resulting plywood. Formaldehyde and dialdehyde starch were used with casein to further improve the water-resistance (Weakley F.B. and C.L. Mehltretter, 1964). However, the treatment of casein with dialdehyde starch significantly increased the viscosity, which made the application of the modified adhesive onto wood furnish difficult (Yang I. *et al.*, 2006). Another undesirable property of casein-based adhesives is that they stain the wood with rich tannic acid (Eckelman C.A., 1997).

Casein-based adhesives were mainly used for laminated lumbers and doors for interior uses (Sellers T., 2001). The wood composite panels bonded with casein-based adhesives have moderate dry shear strength, moderate water- and moisture-resistance and cannot be used for exterior applications.

2.2.1.3 Blood - based Adhesive

Blood can also be used as an adhesive. Blood is a byproduct of slaughterhouse and contains a high amount of protein. Lime and sodium hydroxide are typically used to unfold blood protein for adhesive applications (Eckelman C.A., 1997). Formaldehyde and PF resins were used to improve water-resistance, strength and mold resistance of plywood bonded with the blood-based adhesive (Blomquiest R.F. *et al*., 1981). Blood-based adhesives had a higher moisture resistance, but a lower strength than the casein-based adhesive.

The blood adhesive was used in combinations of PF resins or soybean protein for plywood manufacture (Ash J.R. and A.L. Lambuth, 1957, Golick A.J. and T.W. Dike, 1945). However, it is no longer used in a commercial scale.

2.2.1.4 Soy - based Adhesive

2.2.1.4.1 Production and Composition of Soybean

Soybeans contain about 20% oil, 34% carbohydrates, 40% protein and 4.9% ash (Wolf W.J., 1970). Soybean oil is mainly composed of saturated and unsaturated triglycerides. Soybean carbohydrates consist of the complex polysaccharides including cellulose, hemicelluloses, and pectin. About 18 amino acids can be found in soy protein. Abundant amino acids in soy protein include acidic amino acids (aspartic acid and glutamic acid), non-polar amino acids (alanine, valine and leucine), basic amino acids (lysine and arginine) and uncharged polar amino acids (glycine). Aspartic acid and glutamic acid account for almost 30% of all amino acids in soy protein (Kumar R. *et al*., 2002).

The solubility of soy protein in water is highly dependent upon the pH. In a neutral or alkaline medium, around 80% of the protein can be dissolved (Kumar R. *et al*., 2002).The solubility decreases dramatically in an isoelectric region. The isoelectric region of soy protein is at pH 4.2-4.6. Soy protein can be separated into several fractions with very different characteristics according to their sedimentation constants (Kumar R. *et al*., 2002).The comparison of the fractions in soy protein is shown in Table 2.1.

FRACTION	CONTENT (%)	MOLECULAR MASS (Da)	PRINCIPAL COMPONENT
11S	52	320- 360 k	Glycinin
7S	35	150- 190 k	Beta- conglycinin
15S	5	640- 720 k	Dimer of Glycinin
2S	8	8000- 20,000	Polypeptides

Table 2.1: The comparison of fractions in soy protein

Major commercial soybean products include soybean oil, soy flour, defatted soybean meal, soy protein concentrate (SPC) and soy protein isolate (SPI). Soybeans are typically processed to produce soybean powder through the following steps: cleaning, cracking, dehulling and flaking. Soybean oil is typically removed from the soybean powder through a solvent-extraction process. The commonly used solvent is hexane. Soybean oil can also be removed by squashing soybeans. After the removal of soybean oil, the resulting powder is called defatted soybean meal or soy flour. The defatted soybean meal can be further processed to produce soy protein concentrate (SPC) and soy protein isolate (SPI) through the partial removal of carbohydrates. The protein content for these two products is about 64% for SPC and 90% for SPI (Kinsella J.E., 1979). SPC can be produced through treating defatted soybean meal with three methods: moist heating with water leach, aqueous alcohol washing, and leaching with dilute mineral acid. In these treatments, insoluble SPC is obtained and carbohydrates are removed as the soluble. The following is a typical procedure for production of SPI. Defatted soybean meal is dissolved in warm water at the pH value of 7-8.5, and the insolubles are removed through centrifugation or filtration. The resultant solution is acidified to form precipitate that is further neutralized and dried to generate SPI. The compositions of different soy protein products are shown in Table 2.2 (Kinsella J.E., 1979).