SELINUS UNIVERSITY
OF SCIENCES AND LITERATURE

BIOPOLYMERS IN MATERIAL CULTURE

Use of rigid polyurethane foams in social housing

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Abbreviations

HDPE	High Density Polyethylene
LDPE	Low Density Polyethylene
PP	Polypropylene
PVC	Polyvinyl chloride
LLDPE	Linear low-density polyethylene
VIS	Social housing
AOM	Active oxygen method
HDI	1,6-Hexamethylene diisocyanate
MDI	4,4'-methylenediphenyl diisocyanate
PON	Natural polyols
PU	Polyurethane
PUR	Rigid Polyurethane
CASE	Coating, Adhesives, Sealants and Elastomers
#OH	Number of hydroxyls
PUR's	Rigid Polyurethanes

Summary

Polyurethanes (PU's) are synthetic polymers with versatile properties including good mechanical and chemical resistance, flexibility and good thermal insulation, and can therefore be used in various traditional applications such as foams, coatings and adhesives. Polymers are synthesised through a polycondensation reaction between a polyol and an isocyanate.

Among the synthetic polymers are the PU's that are obtained by means of fossil fuels; however, due to the increase in costs, the damage to the environment that the synthesis of these polymers causes and the scarcity of fossil raw materials that have occurred in recent decades, other renewable sources have been studied in the synthesis of these polymers, incorporating a natural source and thus contributing to sustainable development in the future.

The aim of this work is to validate and cost rigid PURs with mechanical characteristics that allow them to be used as panels in the field of architecture and construction, from natural materials such as vegetable oils and by methods of low environmental impact.

The synthesis of polyols from natural oils was taken from six different routes, which were used prior to this work, referenced as Patents: 2765146 A, US 20140309322 A1, WO/2013/050854, 11201401245S A1 (see Annex 1), authored by the authors. These routes start from the synthesis of polyols and PU's from palm oil, the first route is glycerolysis, the next from transesterification with pentaerythritol, another route from epoxidation of fatty acid methyl esters, the fourth route from maleinated monoglycerides, the fifth from alcoholysis, and a last route from the combination of two previous routes (epoxidation of fatty acid methyl esters and glycerolysis); and thus by comparison of routes more suitable polyols are obtained, from the vegetable source, for the synthesis of PUR's.

The comparison of the polyols was carried out by titration of the hydroxyl groups, under the ASTMD4274-16 standard, obtaining the #OH (mg KOH/sample) of each polyol. The results showed that the polyol with the highest #OH corresponds to the one prepared by route 1: glycerolysis with palm kernel oil, with an #OH value of 523.

The PUR's obtained in the patent showed tensile, compressive and shear strength values, which could be compared; these tests were determined by ASTM standards: D1623-09, D1621-10,

C273, for PUR foams. These mechanical characterisation values showed that through the routes of glycerolysis, alcoholysis and combination of two routes (epoxidation of fatty acid methyl esters and glycerolysis) it is possible to obtain polyols with high #OH value with the two proposed oils, which guarantee PURs with better mechanical resistance.

Subsequently, an evaluation was made, from the laboratory scale, of the costs of obtaining sheets of the different PUR's selected in this work to compare this cost structure in the manufacture of a social housing (VIS) versus the same VIS of traditional manufacture and it was found that the materials synthesised by the proposed methods can be 20% more economically competitive than the traditional material, giving the PUR's obtained from these natural sources a relevant possibility in the market of social housing solutions.

Chapter 1: Introduction

Nowadays, new materials have to comply with ecological requirements with respect to the raw materials used, both in their manufacturing technology and in the elimination of the waste generated, which is why renewable raw materials are attracting the attention of consumers and regulatory agencies. Worldwide, efforts are being made to replace products that deteriorate the environment, either because of the high consumption of non-renewable natural sources or because of the pollution they generate in their manufacture or degradation, with new environmentally friendly products.

The main raw materials for the synthesis of PURs are polyol and isocyanate, which are produced from petroleum derivatives, leading to the consumption of this non-renewable fossil resource at risk of extinction, which is of worldwide interest due to its high energy value (Ng WS, 2017). For this reason, the need to obtain polymeric materials derived from renewable natural sources is becoming increasingly important (Zieleniewska M L. M., 2015). Globally, fossil fuels dominate the world energy market and it is predicted that fossil fuels will continue to produce 75-80% of the world's primary energy by 2030. Global environmental concerns due to their use and finite reserves of these fuels have increased the intention to reduce their consumption in all economic sectors worldwide. (Yang C F. L., 2015)

Recent advances in PUR research have focused on the replacement of polyols and isocyanates of petrochemical origin with molecules of biological origin, as a response to concerns about the depletion of resources and the pollution they generate. The current trend is the use of vegetable oil-based raw materials and the valorization of natural polyols or PONs (Nohra B, 2013). The depletion of natural resources of fossil origin has forced the search for alternative sources of substrates for the production of polymeric materials.

One of the possibilities to increase the environmental performance of polymeric materials is the use of natural substrates from renewable sources in their manufacture. (Bryskiewicz A, 2016)

This work has an antecedent in Patents (Patente nº 2765146 A1), (Patente nº US 20140309322 A1), (Patente nº WO/2013/050854), (Patente nº 11201401245S A1) in which palm oil is used in the synthesis of polyols as an alternative to synthetic polyols, to synthesize PUR's.

2.1. Vegetable oil production in Colombia

Palm oil is the second most harvested vegetable oil in the world, followed by soybean oil; 90% of the world's palm oil production comes from Malaysia and Indonesia.

Palm oil is derived from the fruits of palm bunches, it is semi-solid at room temperature due to the combination of high and low melting point triglycerides and has a red-orange color due to the high amount of carotenes. It is mainly composed of fatty acids, the typical amounts of these acids are: 45% palmitic, 40% oleic, 10% linoleic and 5% stearic. Thanks to its good resistance to oxidation and heating at high temperatures, palm oil is used in various industries for its good performance and economy.

Palm cultivation in Colombia exceeds 500,000 hectares. Palm oil production increased from 15,000 tons in the early 1960s to 232,000 tons in 1989 and to more than 1.7 million tons in 2020, with a production value of around $3.4 billion at present. In the last decade, palm oil production has grown at an average rate of 9.2%, reflecting its dynamism. (aceite, 2018)

In the international context, Colombia is the fourth largest palm oil producer in the world (after Indonesia, Malaysia and Thailand) and the first in the Americas, reaching a yield of 3.9 tons of oil per hectare in 2020, a figure that exceeds the world average and once again positions Colombian palm cultivation at levels similar to those of leading countries such as Indonesia and Malaysia.

In comparison, national soybean production is one of the flags of the government plan Colombia Siembra, which expects an overall increase of one million hectares planted (from 7.13 in 2015 to 8.13 million in 2018) of the country's agricultural supply products. In Colombia there are just over 24,000 hectares planted (2020 figures). The project, at least this year, is to increase the figure to some 37,000 hectares planted with soybeans and move forward (Colombia Siembra expects to increase to 62,000 hectares planted by 2020). (La apuesta por aumentar los cultivos de la soya en Colombia, 2016)

Table 1 shows the production in Colombia of vegetable oils, demonstrating the agricultural importance in the country and the possibility of generating new lines of business with the use of this raw material.

Table 1 National production of vegetable oils in Colombia. (La apuesta por aumentar los cultivos de la soya en Colombia, 2016)

Oil	2020 National Production (Hectares)
Palm	850.000
Palm kernel	370.000
Soybean	37.000
Cotton	150.000

The following figure shows the global projection of bio-based plastics and allows us to understand that the market for these materials may be adequate for the national and international commercial reality.

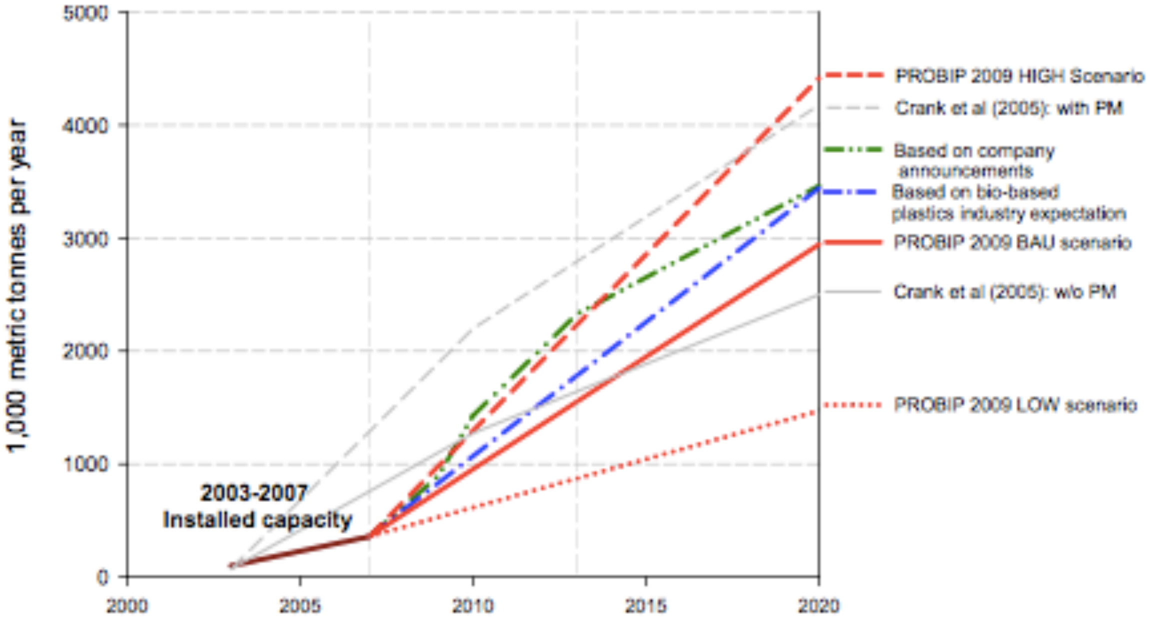


Figure 1 Projected global production capacity for bio-based plastics until 2020. (L. Shen, 2019)

The above Figure 1 shows how PURs occupy an important position in the global market for high performance synthetic polymers. PURs have a global production of 14 Mt and are the sixth most sold plastic in the world, after HDPE, LDPE, PP, PVC and LLDPE, accounting for approximately 6% of total consumption. (L. Shen, 2019)

So far, commercially, the isocyanate component has been derived exclusively from petrochemical feedstock; however, the polyol component can be produced from renewable resources such as soybean oil, castor oil, sunflower oil, and rapeseed oil, among the commercially most important. (L. Shen, 2019)

Depending on the sources of origin chosen, the renewable content of commercially available plant-based polyols varies between 30 and 100%. Consequently, the renewable content of PURs based on different formulations also varies substantially among different products and applications, with a range of 8-70%, as shown in Table 2

Table 2 Renewable content of commercially available bio-based polyols and PUR´s (L. Shen, 2019).

Renewable source of polyol	Bio-content of polyols	Bio-content of PUR
Sucrose (polysaccharides)	≤ 30%	< 8% (rigid foam)
Soybean seed	40 -100%	5 – 60% (Flexible and rigid foam, CASE)
Castor oil	30 – 100%	22 – 70% (Flexible and rigid foam, CASE)
Sunflower oil	n/a	≥ 25% (Flexible foam)
Corn oil (polysaccharides)	100%	n/a

Based on different formulations, PUR's cover a wide range of stiffness, hardness and density and commercial applications can be classified into three general ones: rigid foams, semi-rigid foams and flexible foams, as shown in Table 2.

2.2. Demand for construction materials in Colombia

In recent years, Colombian cities have grown considerably, following a pattern of metropolization and compaction. Habitat solutions for housing have shown a notorious participation of low-quality settlements.

Recognizing the dynamics of housing production in Colombia, the application of family subsidy resources is contemplated, focused on: the construction of housing units, acquisition of lots, construction of basic units and progressive housing, acquisition of materials for the improvement of housing and the environment, legalization of titles and acquisition of used housing. This diversity of options allows each family to seek the scenario that best suits their needs and expectations.

The challenge is to respond in a flexible manner to this type of needs with different architectural programs for housing and with progressive schemes that meet the specific needs and possibilities of each one, understanding that in this country 87% require low-cost housing and with a great versatility in the decrease of its structure. (2015-2016., 2018)

In Colombia, the National System of Social Interest Housing (VIS) was created whose sole purpose is to generate public-private alliances that facilitate the development of activities that are necessary to provide the salaried population belonging to that 87% of a country of approximately 50 million census inhabitants, the possibility of accessing the construction or improvement of housing in accordance with the basic needs of dignity, freedom and egalitarian growth. (Escallón, 2021)

By 2016, houses of 30 square meters were delivered to peasant families, in addition, the Government went on to finance the projects at 100 percent, that is, 30 percent more than in 2014. There are currently 26,729 rural social interest housing subsidies allocated, with a total budget of 767,962 million pesos.

The housing deficit is more than 3 million homes, in addition to the housing affected by the winter waves of some years ago. This is a challenge that cannot be met with new and finished housing alone. Therefore, the focus must be on quality and habitability, allowing for safe housing that meets the appropriate urban standards. (DANE, 2019)

The proposal with the materials developed in this work is to propose a viable alternative based on palm oil resources, among others, (abundant in national crops) for the development and compensation of social housing with significant savings in the structuring of housing without affecting the minimum required by the national construction system. And it is specifically oriented in the generation of housing modules according to standard specifications. For a type of VIS housing.

Figure 2 VIS in the Colombian Caribbean zone

The industrialization of PUR in Colombia is highly developed given the low industrial assembly requirements, therefore, it is easy to make a comparison between the manufacturing (in costs) of a PUR sheet obtained from petrochemical sources and those proposed in this work. This comparison was made under the premise of sheets of 2 m x 2.5 m in length and width, and a thickness determined by the mold of 20 cm according to the technical considerations for the application in VIS (Escallón, 2021).

There are many examples of PUR applications in the manufacture of social housing or transitory spaces, for example, a PU sheet for the industrial sector marketed by “Industrias JQ” (Buenos Aires- Argentina) must have a tensile strength greater than 4.36 kg/cm2 established under ASTM D-638 and a compressive strength of 2.5-4.3 kg/cm2 established under ASTM D-695 and a shear strength of 4.56 kg/cm2 established under ASTM standard.

Different types of polymers are used in construction; one of them is polyisocyanurate, which has physical and chemical properties very similar to polyurethane. According to the company “Espumlatex”, this material must have a compressive strength greater than 172 kPa, which is determined according to ASTM D-1621.

According to theoretical sources, the compressive strength of a 30 kg/m3 PU foam should be 130 kPa and 325 kPa for a density of 60 kg/m3, and the tensile strength of a 30 kg/m3 foam should be 180 kPa and 820 kPa for a density of 60 kg/m3.

In comparison, the data of elastomers positioned in the market such as Fluoroelastomer (FKM)-Viton presents a tensile strength of 11.3 MPa, Ethylene-propylene rubber (EPDM) has a tensile strength of 5.5 MPa and Styrene- Butadiene Rubber (SBR) with a tensile strength of 7MPa.

2.3. Patents obtained (field of invention) (see Annex 1)

Prior to this work, a project was developed with the objective of obtaining polyols and PUR foams from palm oil, to generate a commercial line on these new materials, with uses in: manufacture of housing partitions, insulation and refrigeration systems and integration of parts for automobiles, trains, airplanes and the aerospace industry. The project resulted in the patents listed in Table 3.

Table 3 Previously obtained patents

Patents obtained
2765146 A1 - Processes for obtaining a polyol from palm oil, polyols obtained from said processes, products derived from said polyol and method for preparing same
US 20140309322 A1 - Processes for obtaining a polyol from palm oil, polyols obtained from said processes, products derived from said polyol and method for preparing same
WO/2013/050854 - Procesos para la obtención de un poliol a partir de aceite de palma, polioles obtenidos a partir de dichos procesos, productos derivados de dicho poliol y su método de preparación
11201401245S A1 - Processes for obtaining a polyol from palm oil, polyols obtained from said processes, products derived from said polyol and method for preparing same

The invention recognized in the patents relates to the process for the production of a polyol from palm oil and to PUR foams prepared from said polyol derived from palm oil. On the one hand, the present invention provides a method for obtaining monomeric polyols obtained from palm oil and having hydroxyl number between 50 and 450 mg KOH/g sample. The polyols of the patents are obtained by means of a procedure based on the following four fundamental routes:

- Route 1: maleinization of palm oil fatty acids;
- Route 2: glycerolysis of palm oil;
- Route 3: palm oil transesterification; and Route 4: palm oil epoxidation.
- Route 4: epoxidation of the unsaturated carbon-carbon bonds of palm oil.

Additionally, other embodiments of the invention allow the obtaining of polyols from the combination of these fundamental routes.

In another aspect of the invention polyurethanes are prepared from the polyols obtained by any of the four routes or by a combination thereof. In one embodiment of the patent the polyurethanes are produced by reacting a mixture of a polyol obtained from a commercial polyol, a surfactant, a catalyst and an isocyanate. The polyurethanes obtained are high density rigid foams.

Although the previous state of the art has sought solutions to the technical problem, which is to provide methods for obtaining "green" polyols, i.e., from vegetable oils including palm oil, as well as obtaining PUfoams from these "green" polyols with properties that allow their application in the different uses mentioned above, None of the documents found refer to a procedure for obtaining polyols derived from palm oil used for the preparation of polyurethane, where two preparation methods are combined, providing greater functionality to the final molecular structure. This allows improving the characteristics of the PUobtained from said polyol, giving it properties such as: greater functionality and greater crosslinking.

Although in other inventions polyols have been obtained from vegetable oils, the products prepared from such polyols are brittle due to the concentration of hydroxyl groups at only one end of the carbon chain.

Additionally, and in relation to the operating conditions of the glycerolysis method, in the present invention it was possible to reduce the reaction temperature to obtain the polyol with favorable results with respect to the reduction of energy costs.

The invention provides a simple method in its realization, of low cost with respect to the traditional obtaining, and gives as final result a product of high technical and functional qualities that places it above those that, of conventional type and within the same line are found in the previous state of the art, with the advantage of having within its raw materials a polyol from renewable natural sources.

By means of the invention polyols with molecular weights between 314 and 3366 and with hydroxyl numbers between 50 and 450 mg KOH/g of sample are obtained.

The resulting rigid foams were tested for: density (according to ASTM C373-88) with results between 0.284 and 0.658 g/cm3, Young's modulus (according to ASTM D695-10) with results between 8.95 and 54.92 MPa and maximum stress (according to ASTM D695-10) with results between 0.92 and 8.29 MPa, determining a high functional performance material for its petrochemical counterparts in the market.

Chapter 2: Statement of the problem

2.4. Justification of the research

In order to determine to what extent housing needs are satisfied, two factors are taken into account, the first is the quantitative deficit which estimates that a measure of the amount of existing housing is insufficient to house the entire population of the country, secondly the qualitative deficit is taken into account, which measures the number of homes that do not meet minimum quality standards such as availability of public services or mitigable space (more than three and less than five people per room). (DANE, 2019)

The quantitative deficit estimates the amount of housing that must be built so that there is a relationship between adequate housing and families in need of shelter, in addition, this deficit takes into account families that are housed in natural shelters or under bridges without stable walls or of precarious material. For this study, the quantitative housing deficit figure in Colombia will be taken into account. (DANE, 2019)

According to the Ministry of Housing, in Colombia this deficit decreased by 7%, i.e. from 12.6% in 2010 to 4.6% in 2020. On the other hand, the DANE reports in the national population and housing census conducted in 2020 that there are 14'000,000 families in the country, so 770,000 households are in precarious housing conditions, therefore, this amount should be built to mitigate the current quantitative deficit in Colombia.

2.5. Technology watch

Both polyols of vegetable origin and PUR's synthesized from these polyols have been a topic of interest in the last 10 years, particularly for the countries with the highest production of these vegetable oils. Thus, Colombia, from its privileged position in the production of these oils, is trying to take advantage of their characteristics to solve basic problems of the population, including housing, as a priority issue.

In order to understand the dynamics of research, patents and trademarks that allow us to have a vision of the technological surveillance of the topic, bibliometrics and scientometrics of the topics worked on were carried out according to Tables 4 and 5.

2.5.1. Polyols of vegetable origin

The basic data of the search for information on the research on polyols of plant origin and the summary graph of this search are shown in Table 4 and Figure 3.

Table 4 Technical information on technology watch research on polyols from vegetable oils.

Source: Web of Science ,2019 and VosViewer
Total of Articles published in indexed sources: 1140
Search equation: polyol and natural oils
Date of update: March 05, 2019

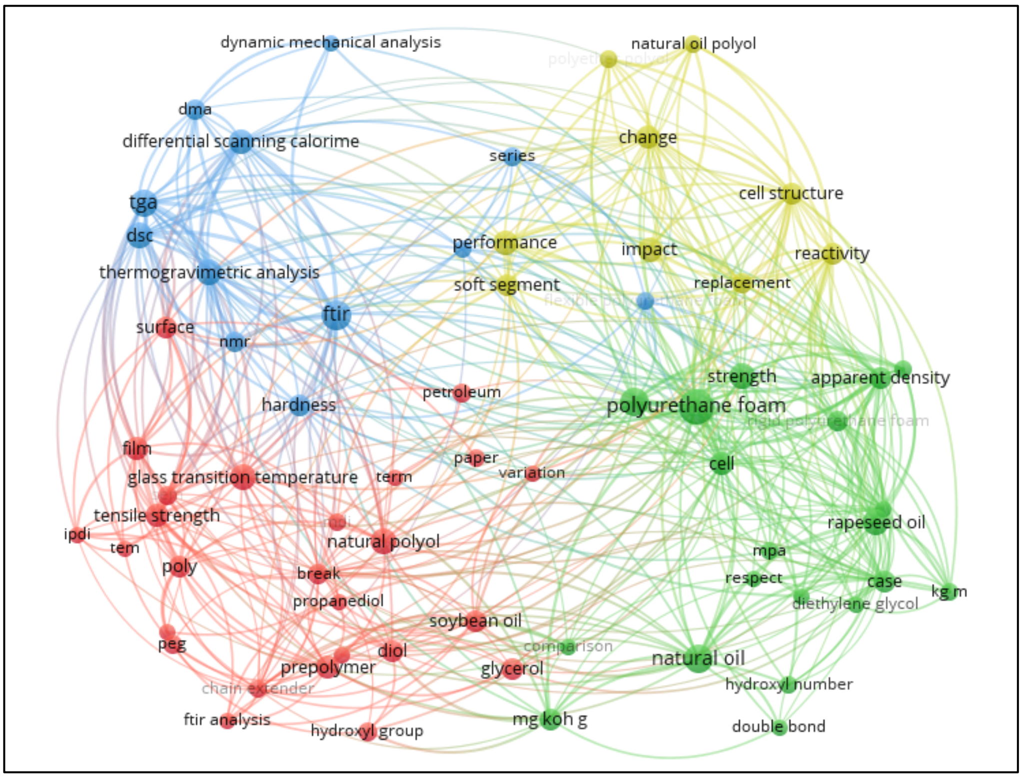


Figure 3 Relationship between article titles and patents on vegetable oil polyols and PURs from natural sources.

Figure 3 shows that the largest trends in publications are on: PUfoams, PON's and Natural oils, with these publications having a direct relationship of citations and referencing. This shows us the relevance of the topic, especially when working on non-conventional oils for the PUR industry and applications that allow mass solutions for the material.

Table 5 Technical information on the technological surveillance of patents on polyols and PURs from vegetable oils.

Source: *Derwent Innovations Index,* Web of Science ,2019
Total Patents published in indexed sources: 151
Search equation: polyol and natural oils
Date of update: March 05, 2019

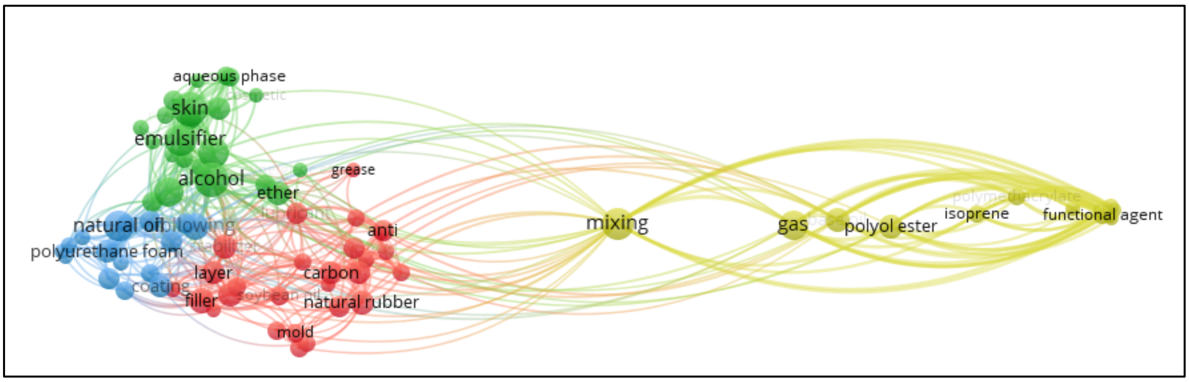


Figure 4 Patent management on polyols and polyurethanes from vegetable oils

Figure 4 shows that the biggest trends in patents are on: Vegetable oils, PU foams and Carbon blends. This shows the relevance of the topic, especially when working on non-conventional oils for the PUR industry and their functionalization to innovate in applications with high social impact.

Table 6 shows the list of brands, applications, biological origin and other elements in the PUR market, which is currently evolving at international level on material improvements, new applications and original bio-based sources.

Table 6 Raw material, trade names and main producers of bio-based polyols and PUR´s (L. Shen, 2019).

Bio-based raw material	Marketed	Trade name	PUR application	Company
Soybean oil	Polyol	BiOH ™	Flexible foams	Cargill
	Polyol	Renueva ™	Flexible and CASE foams	Dow
	Polyol	SoyOyl ©	Flexible and rigid foams, PUR Spray Foam	Urethane Soy System
	Polyol PUR	Agrol Bio-based	CASE, Moulded foams	Bio-based Technology
	PUR	Baydur	Rigid and Flexible Foams	Bayer
Castor Oil	Polyol	Lupranol BALANCE	Rigid foams / mattresses	BASF
	Polyol	POLYCIN	Coatings	Vertellus
	Polyol PUR		Rigid and flexible foams	Mitsui Chamicals
Sunflower oil	PUR	LUREX NAWARO	Flexible foams / Mattresses	Metzeler Schaum
Maicena	Polyol	Cerenol TM	Elastomers and spandex fibres	DuPont
Unknown	PUR (TPU)	Pearlbond ECO	CASE / Electronics / Footwear	Merquinsa

2.6. Problem Faced by the Industry Due Phase out Schedule

The processing and application of rigid foams obtained from oil have faced many problems due to the environmental requirements for their possible alternative uses. These problems include:

- Dimensional stability of the foam
- Blend stability
- Foam flowability
- Blend viscosity
- Foam friability
- d) Substrate adhesion to the foam
- Cost

- Temperature resistance
- Insulation performance of the foam
- K-factor aging
- Blowing agent solubility
- Flammability of the liquid blend.

This is why obtaining and applying PUR from renewable sources generates a high impact on its commercial versatility.

2.7. Research Objectives

2.7.1. General Objective

To evaluate the advantage of the application of PURs from renewable sources, from their mechanical characteristics, according to the requirements of the construction sector in Colombia, in VIS as a commercial alternative.

2.7.2. Specific objectives

- Define the chemical and mechanical performance of PUR obtained from natural oils for commercial structural use.
- To evaluate the cost of application of PUR obtained from renewable sources in VIS.

Chapter 3: State of the Art

The development of PUR began in the 1940's with the work of Otto Bayer and collaborators, when they reacted a polyol and a diisocyanate to obtain the first PUR with excellent adhesive properties. PUR's are plastic polymers widely used in modern life, today they are one of the most versatile materials in existence; due to their physical properties and versatility, their applications range from flexible foam used in furniture and mattress upholstery, to rigid foam used as insulation in walls and ceilings. In addition to thermoplastic materials used in medical devices, footwear coatings, adhesives, sealants and elastomers used in flooring and automotive interiors. Depending on the application, one of the raw materials of PUR can have its density and stiffness varied to achieve the desired product performance. (Nohra B, 2013), (R., 2009), (García DE, 2015)

The reagents used in the synthesis of polyurethanes are very varied, which allows their diverse properties to be obtained. In the synthesis of straight-chain thermoplastic elastomeric polyurethanes there are three: a high molecular weight bifunctional polyol, a diisocyanate, and a low molecular weight bifunctional diol. In addition to these three basic components, different types of catalysts and additives are also used for the improvement of the processing or properties of the PU according to the desired application. (Cauich Rodríguez J V, 2019)

3.1. Macrodiols - polyols

The polyols used in the synthesis of polyurethanes are relatively large molecules, of molecular weight between 500-4000 g/mol, which must be bifunctional (molecules with two reactive centers) to obtain linear polyurethanes.

The polyol constitutes 50 to 80% of the mass of the PU and has a significant influence on its final properties. Macrodiols form the flexible segment of the polyurethane, provide the elastomeric properties, and control the low-temperature properties. Polyetherdiol and polyesterdiol macrodiols are commonly used; in recent years, other types of macrodiols have been tested in order to obtain better properties. Figure 6 shows the chemical structure of the most commonly used macrodiols in the synthesis of polyurethanes. (Cauich Rodríguez J V, 2019)

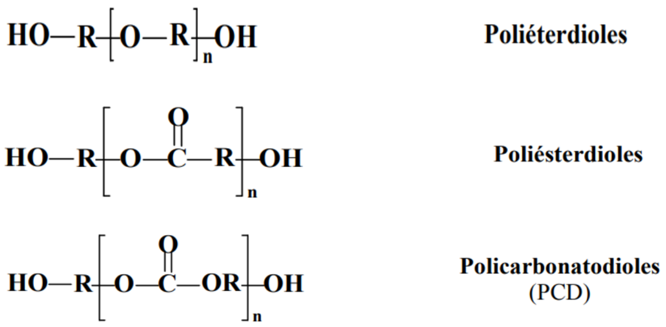


Figure 5 Chemical structure of the macrodiols most commonly used in the synthesis of polyurethanes.

The polyetherdiol type macrodiols are low cost and easy to handle, among them is propylene glycol, which is obtained by catalyzed reaction of propylene oxide bases.

Polyesterdiols are more expensive than polyetherdiols but have higher viscosity, low resistance to hydrolysis and high temperature resistance; they are obtained by polycondensation reaction between polyols and dicarboxylic acids.

Finally, there are the polycarbonatodiols that are obtained by polycondensation of diols and phosgene and by transterification of diols and carbonates; these present greater resistance to hydrolysis, to degradation by ultraviolet radiation, oxidizing atmosphere and solvent with respect to the two previous macrodiols. (Cauich Rodríguez J V, 2019)

3.2. Obtaining polyols from natural oils

Polyols can be synthesized from natural raw materials such as plants, oils and wood. In the polymer industry, different types of oils (castor, soybean, rapeseed or canola) have been employed as raw materials due to their variety and economy (Pillai PKS, 2018). Vegetable oils are the most promising, as they are cheap, readily available and are renewable resources (Cauich Rodríguez J V, 2019), (Pillai PKS, 2018). Vegetable oils are triglycerides of saturated and unsaturated fatty acids (Figure 6). The six most common fatty acids are:

- Palmitic (C16:0)
- stearic (C 18:0)

- Oleic (C 18:1)
- Linoleic (C 18:2)
- Linoleic (C 18:3)
- Ricinolenic (C18:1OH)

Note: In this notation, the first number represents the number of carbon atoms, the second number represents the number of carbon-carbon double bonds and the OH represents the hydroxyl groups in the fatty acid.

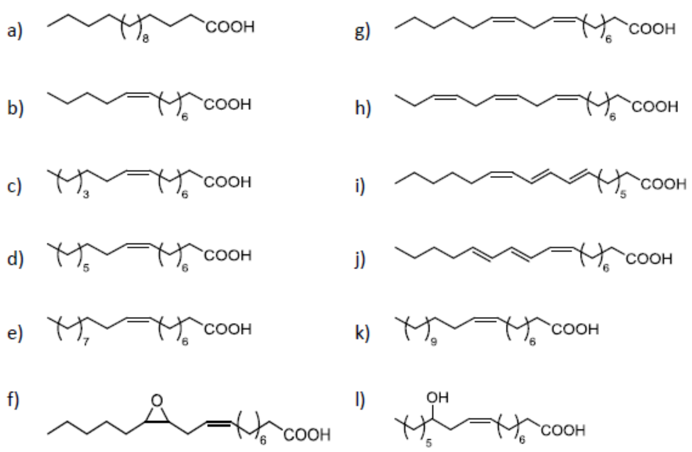
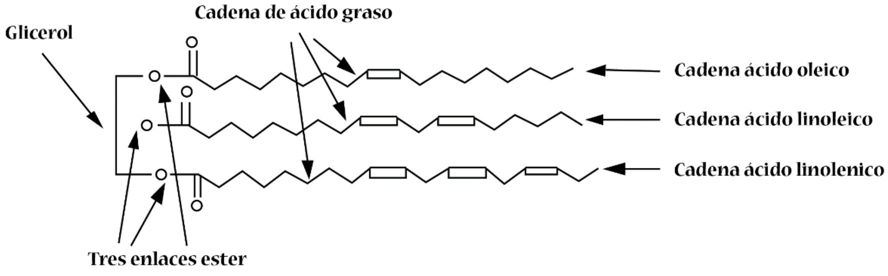


Figure 6 Structure of the fatty acids of greatest interest: a) palmitic acid, b) myristic acid, c) palmitoleic acid, d) oleic acid, e) gadoleic acid, f) vernolic acid, g) linoleic acid, h) linolenic acid, i) calendic acid, j) α-eleostearic acid, k) erucic acid, l) ricinoleic acid.

These fatty acids are found in different composition depending on the plant from which the vegetable oil is obtained, as well as the growing conditions of the plant. The fatty acid composition of each oil affects both its chemical and physical properties.



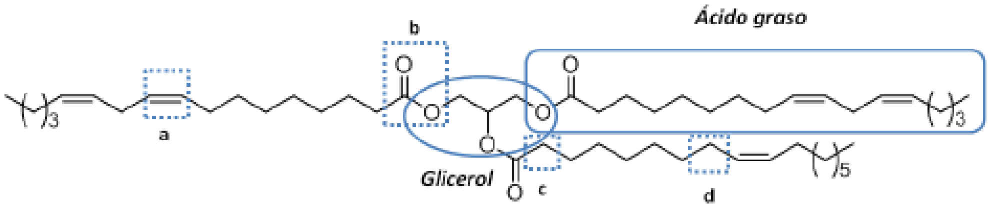


Figure 7 General structure and reactive positions of triglycerides (in this example, with oleic acid and linoleic acid): a) C-C double bond, b) ester group, c) α-position to the ester group, d) allylic position.

The double bonds of oil triglycerides are of utmost importance because these are transformed to hydroxyls by means of an epoxidation reaction, so it is necessary to use oils with the highest possible content of unsaturated fatty acids. Among the oils studied in polymer production are cottonseed, safflower, corn, soybean, castor and palm oil, among others.

Tables 7, 8 and 9 show the composition of some vegetable oils, i.e., those obtained from seeds or other parts of plants, the properties and information on the fatty acids of which they are composed.

Table 7 Composition of some vegetable oils

Characteristic	**Cotton**	**Maize**	**Safflower**
Colour	50 yellow/4.0 red máx.	15 yellow/1.5 red máx.	35 yellow/4.5 red máx.
Iodine value	99 – 119	136-148	107 -135
Free fatty acids	0.05% máx.	0.05% máx.	0.10%
Oleic acid	14.7 - 21.7	8.4 -30.0	20 – 42.2
Linoleic acid	46.7 – 21.7	67.8 – 83.2	39.4 – 65.0
Palmitic acid	21.4 – 26.4	5.3 – 8.0	9.2 – 16.5
Stearic acid	2.1 – 3.3	1.9 -2.9	0 – 3.3
Peroxide value	2.0 máx.	20. máx.	20. máx.
AOM Stability	15 – 25 hours.	10 hours min.	10 hours min.
Appearance	crystalline	crystalline	crystalline

Table 8 Properties of vegetable oils

Aceite	**Punto de fusión (º C)**		**Punto de solidificación (º C)**	**Índice de saponificación (º C)**	**Indice de refracción**	**Índice de yodo**	**Ácidos grasos libres oléicos (%)**	**Peso específico**	**Materia no saponificable**	**Color**
	Fusión incipiente	**Fusión completa**								
Coco	20 - 22	23 - 26	22 - 23,5	225 - 264	13 - 10,5	7 - 10,5	3 - 5	0,869 - 0,874	0,15 - 0,8	Blancuzco
Palmiste	21 - 24	26 - 29	24 - 26,5	242 - 255	35,3 - 39,5	14 - 23	2 - 3	0,859 - 0,973	0,2 - 1,0	Blancuzco
Palma	20 - 40	25 - 50	25 - 40	197 - 202	39 - 49	49 - 57	2 - 5	0,921 - 0,925	0,5 - 2,0	Naranja
Oliva	-	-	0 - 7	188 - 196	51 - 57	79 - 88	1 - 8	0,914 - 0,919	0,5 - 1,8	Verdoso
Cacahuate	-	-	0 - 3	188 - 195	51,7 - 57,9	82 - 100	0,4 - 1,6	0,917 - 0,921	0,4 - 1,0	Amarillo dorado
Colza	-	-	(-10) - (-12)	168 - 180	57,1 - 63,2	97 - 108	0,9 - 1,2	0,913 - 0,918	0,6 - 1,5	Amarillo parduzco
Sésamo	-	-	(-3) - (-4)	188 - 195	57,7 - 63,8	103 - 118	0,7	0,920 - 0,926	0,8 - 1,8	Amarillo claro
Soya	-	-	(-7) - (-12)	189 - 195	59,4 - 69,5	120 - 143	0,8 - 1	0,924 - 0,928	0,7 - 1,6	Marrón rojizo
Algodón	-	-	(-5) - 5	189 - 198	57,9 - 63,8	99 - 114	1,1	0,921 - 0,925	0,8 - 1,8	Negro
Maiz	-	-	-	-	-	-	-	-	-	-
Girasol	-	-	-	183 - 194	60 - 63,5	120 - 140	1,1 - 2,7	0,922 - 0,926	0,3 - 1,5	Amarillo dorado
Cártamo	-	-	-	188 - 194	61,7 - 64,8	135 - 150	2,8	0,915 - 0,928	0,5 - 1,5	Naranja amarillento
Linaza	-	(-16) - (-20)	-27	188 - 196	69,5 - 79	175 - 204	1	0,931 - 0,938	1,0 - 1,7	Pardo
Higuerilla	-	-	-	176 - 187	60,2 - 71,9	80 - 91	1 - 4	0,958 - 0,969	0,3 - 1,0	Amarillo claro

Table 9 Fatty acids present in vegetable oils

Aceite	**Proporción Insat/Sat.**	**Saturada**					**Monoinsaturada**	**Poliinsaturada**		**Composición**		
		Ácido cáprico C10:0	**Ácido láurico C12:0**	**Ácido mirístico C14:0**	**Ácido palmítico C16:0**	**Ácido esteárico C18:0**	**Ácido oleico C18:1**	**Ácido linoleico (ω6) C18:2**	**Ácido α-linoleico (ω6) C18:3**	**Contenido de aceite del material oleaginosos (% en peso)**	**Principal ácido graso**	**Contenido del principal ácido graso (% en peso)**
Coco	0,1	6	47	18	9	3	6	2	-	65 - 68	Láurico	44 - 52
Palmiste	0,2	4	48	16	8	3	15	2	-	45 - 50	Láurico	46 - 52
Palma	1	-	-	1	45	4	40	10	-	45 - 50	Palmítico	32 - 47
Oliva	4,6	-	-	-	13	3	71	10	1	15 - 40	Oléico	65 - 86
Cacahuate	4	-	-	-	11	2	48	32	-	45 - 55	Oléico	42 - 72
Colza	15,7	-	-	-	4	2	62	22	10	40 - 50	Behenico, euricico	48 - 60
Sésamo	6,6	-	-	-	9	4	41	45	-	44 - 54	Oléico	34 - 45
Soya	5,7	-	-	-	11	4	24	54	7	18 - 20	Linoléico	52 - 60
Algodón	2,8	-	-	1	22	3	19	54	1	15 - 24	Linoléico	40 - 55
Maiz	6,7	-	-	-	11	2	28	58	1	33 - 39	Oléico, linoléico	34 - 62
Girasol	7,3	-	-	-	7	5	19	68	1	22 - 36	Linoléico	58 - 67
Cártamo	10,1	-	-	-	7	2	13	79	-	25 - 44	Linoléico	78
Linaza	9	-	-	-	3	7	21	16	53	35 - 44	Linoléico	30 - 60
Higuerilla	-	-	-	-	1 - 2	1 - 1,5	3 - 3,5	3 - 4,2	0,3 - 0,5	35 - 55	Ricinoléico	80 - 90

The number of double bonds in the fatty acids of natural oils is of utmost importance for their application in PU synthesis, as these groups are responsible for the formation of cross-links during the formation of the cross-linked polymer. The degree of saturation is typically expressed by the iodine value, i.e. the amount of iodine in grams with which the double bonds present in 100 g of sample can react. According to the iodine value, vegetable oils are divided into three classes: dry (iodine value >150), semi-dry (150>iodine value>120) and non-dry (iodine value<120). (Zieleniewska M L. M., 2018)

There are different references that give evidence of the effort that has been made to obtain PURs with good properties from natural sources (Alam, 2019), (Latere Dwan'isa JP, 2016). Thus, PUR's have been obtained by the solvent-free catalyst method, to prepare a series of polyols from vegetable oils of olive, canola, grape seed, linseed, and castor. (Gindl W, 2016).

PUR's derived from vegetable oils are also found blended with other materials to improve their properties; For example, the properties of PURs from soybean oil can be improved by introducing fiber reinforcements into the polymeric matrix, thus creating a composite material (Zlatanic, 2017). Some studies show improved properties of PUR's with the use of glass fibers and natural fibers (Alam, 2019), (Latere Dwan'isa JP, 2016), (Seydibeyoğlu MÖ, 2018), (Husic S, 2018). Among the reinforcing materials used, cellulose fibers, especially nanocellulose fibers, are attracting much attention (Zlatanic, 2017), e.g., reinforcing PUR with cellulose nanofibers results in a composite material with enhanced crystallinity and tensile strength. (Zlatanic, 2017).

The physicochemical properties of PONs depend on two main parameters: the chosen vegetable oil and the synthesis route. Each vegetable oil has its own fatty acid profile, which can vary depending on the geographical location of the crop and the year of harvest, to have a standard range of PONs would require standardization of the crop to ensure homogeneity of the vegetable oil. Each chemical route provides a PON with different chemical structures (number and position of hydroxyl groups, side chains and molecular weight) and physical properties (viscosity, solubility), which affects its reactivity. Therefore, accurate characterization is required before its use as a reagent. (Weißenborn O, 2016)

Several routes can be employed for the synthesis of polyols derived from natural oils, among which are:

3.2.1. Epoxidation route.

Vegetable oils are epoxidized, and the epoxide formed is opened by the addition of various proton donors such as alcohols. The use of alcohols such as methanol is particularly preferred, since it yields liquid polyols with a large number of functional groups. However, by this route only secondary hydroxyl groups are generated, resulting in a lack of reactivity with isocyanates. On the other hand, hydroxyl groups are present in the middle of the aliphatic chains, which are not included in the polymeric network after reaction with isocyanates, resulting in a less rigid PUR. (Buschow KHJ, 2018)

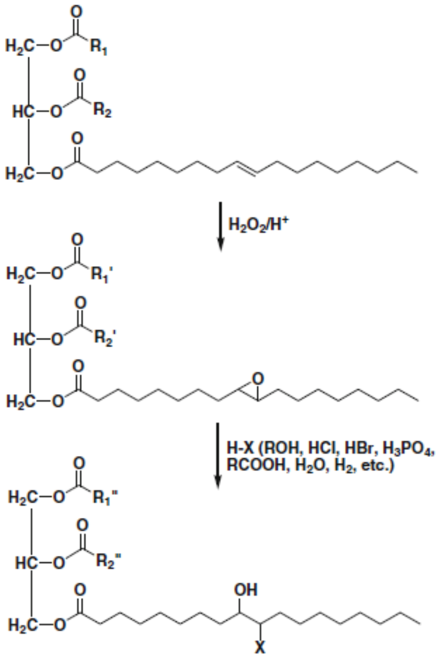


Figure 8 Epoxidation reaction in polyols.

Production of vegetable oil-based polyols occurs via epoxidation and oxirane ring opening pathway where R1 and R2 are vegetable oil fatty acid side chains, R1 ', R2', R1 "and R2 " are modified vegetable oil fatty acid side chains.

3.2.2. Reduction / hydroformylation route

The introduction of a primary hydroxymethylated group to the ethylene functional group is achieved by a two-step reaction with high-cost catalysts.

The treatment of the vegetable oil is done with synthesis gas, to obtain a further reduced aldehyde by hydrogen gas and the resulting PURs are always amorphous or crystalline materials, because of the loose chains within the polymeric matrix. (Buschow KHJ, 2018)

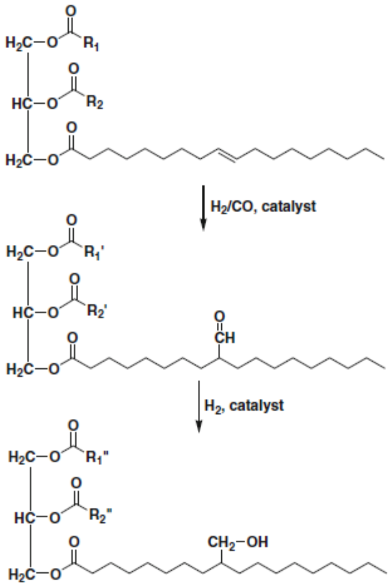


Figure 9 Hydroformylation reaction in polyols.

In the production of vegetable oil-based polyols by the hydroformylation and hydrogenation route R1 and R2 are fatty acid side chains of vegetable oils; R1 ', R2', R1 "and R2 " are modified fatty acid side chains of vegetable oil.

3.2.3. Ozonolysis/Reduction route

In this route, the carbon-carbon double bond is cleaved in three steps to obtain terminal primary hydroxyl groups; the vegetable oil is treated with ozone to obtain an ozonide, which is reduced to an aldehyde and then to an alcohol. Since they remain free of loose chains, the resulting polyols have higher Tg and better mechanical properties. (Buschow KHJ, 2018)

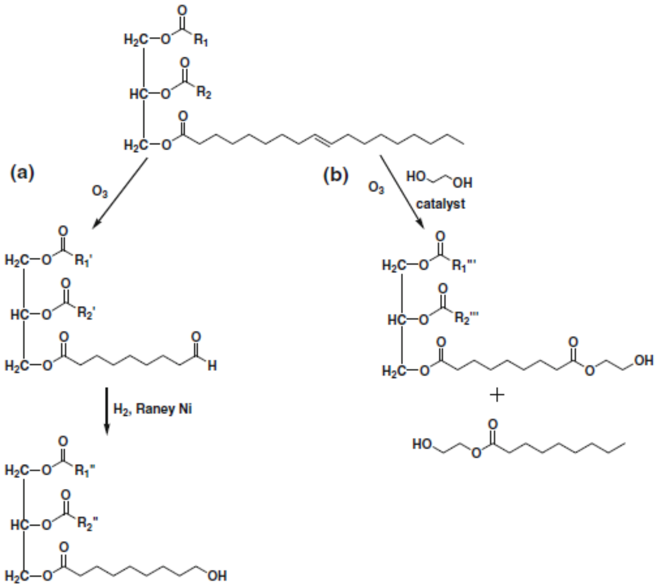


Figure 10 Ozonolysis reaction in polyols.

In the production of vegetable oil-based polyols by ozonolysis and hydrogenation route (a) and ozonolysis route with the addition of ethylene glycol (b), R1 and R2 are vegetable oil side chains of the vegetable oil; R1 ', R2', R1 ", R1 ", R2 ", R1" and R2 "are modified fatty acid side chains of vegetable oil.

3.2.4. Transesterification route

All vegetable oils can be transesterified in the presence of bases or enzymes as catalysts, to form polyols, preferably polyols without β-hydrogen (pentaerythritol and trimethylolpropane), which have higher chemical and thermal stability. Diethalonamines can also be obtained by amidation of vegetable oils with ethanolamine. In both cases, the fatty acid chains can act as plasticizers, which tends to weaken the mechanical properties of the resulting PUR. (Buschow KHJ, 2018)

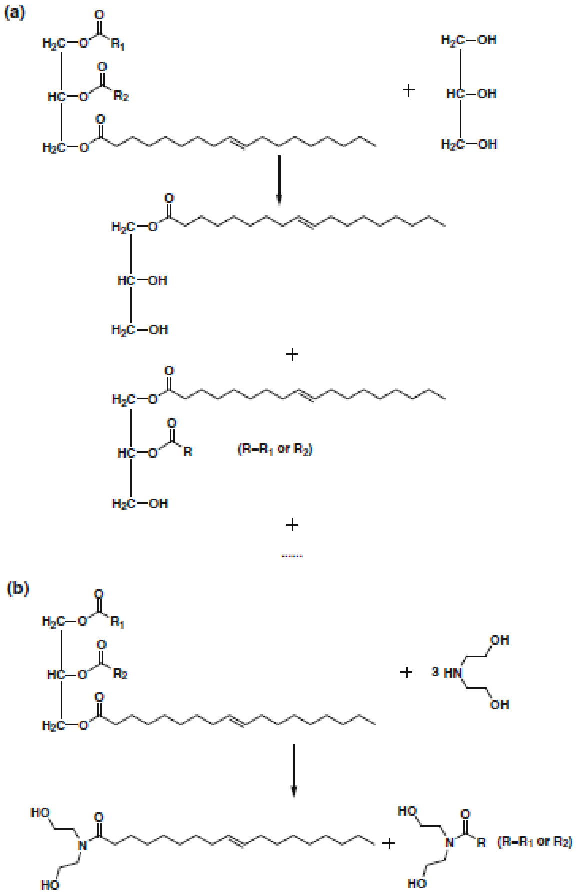


Figure 11 Transesterification reaction in polyols.

In the production of vegetable oil-based polyols by transesterification with glycerol (a) and amidation with diethanolamine (b), R1 and R2 are side chains of vegetable oil fatty acids).

3.2.5. Methathesis Route

Long-chain fatty acid diols can be obtained in two steps, starting with a metathesis reaction and followed by a reduction reaction, with ruthenium as catalyst. (Buschow KHJ, 2018)

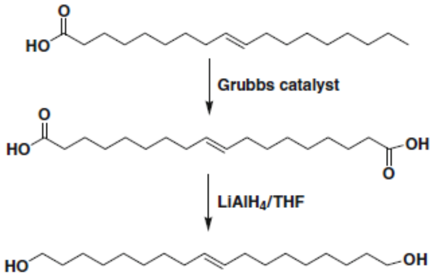


Figure 12 Metathesis reaction in polyols.

3.3. Diisocyanates

Diisocyanates are composed of two cyanate groups (-N=C=O). The structure of this group influences the properties of the final polyurethane, such as rigidity, high melting point and crystallinity. Diisocyanates are classified into aliphatic and aromatic diisocyanates, the latter being the most used due to their low cost, higher reactivity and higher polymerization reaction speed, in addition, aromatic diisocyanates have better mechanical properties, such as: higher deformation and tensile strength, higher ductility and higher thermal resistance; all of the above in comparison with aliphatic diisocyanates. However, there are some disadvantages of aromatic diisocyanates with respect to aliphatic ones, one of them is the instability to light for being a cyclic compound and having its double bonds conjugated, which makes the compound change its physical appearance and turn to a yellowish color that can be a sign of the loss of thermal stability of the material. (Li Y. L., 2015)

During the synthesis of polyurethanes, diisocyanates are responsible for chain extension and the formation of urethane bonds and a variety of cross-links by further reaction.

Figure 14 shows the chemical structure of the most commonly used diisocyanates in the synthesis of polyurethanes.

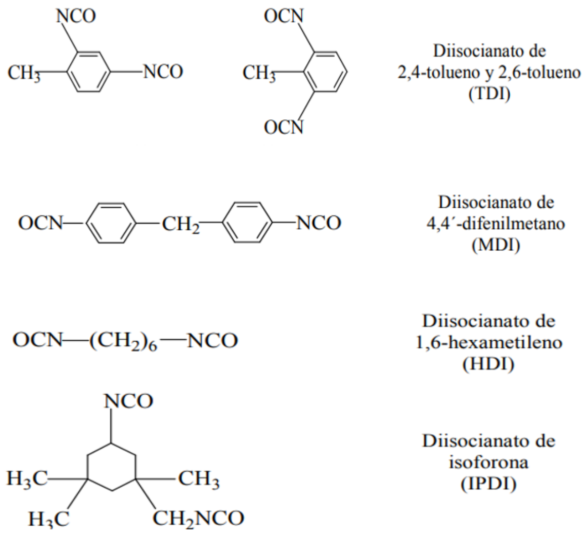


Figure 13 Structure of the diisocyanates most commonly used in PU synthesis.

Toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI) are some examples of aromatic structures of this group, while hexamethylene diisocyanate (HDI) and isophorone diisocyanate belong to the aliphatic group. TDI is a colorless liquid at room temperature with low cost, low viscosity and has high volatility, which implies toxicity problems, while MDI is white flake solid, less volatile, fast reacting and can be dimerized at room temperature; the latter can be found as the polymeric MDI, which is used to manufacture rigid and semi-PUR foams and the monomeric MDI which is used to synthesize flexible polyurethanes and thermoplastics. (Li Y. L., 2015)

3.3.1. Isocyanate chemistry

The chemistry of PU focuses mainly on the reactivity of the isocyanate group as it has different resonant structures, one of the most important reactions is nucleophilic addition due to the electrophilic character of the -NCO group. Figure 15 shows the behavior of the resonant structures of the isocyanate group.

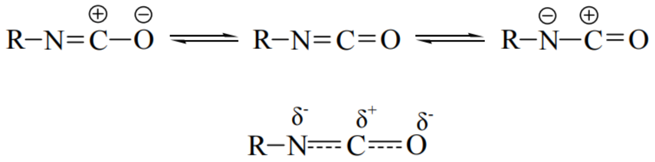


Figure 14 Resonant structures of the isocyanate group.

The chemical difference between aliphatic and aromatic isocyanates lies in the fact that the latter have greater reactivity due to the electronic delocalization of the negative charge in their rings, which increases the electrophilic character of the -NCO group. The reaction occurs when the substituents of the aromatic ring accept negative electrons; on the contrary, if they are electron givers, the electrophilic character and therefore the reactivity of the isocyanate decreases.

For the synthesis of polyurethanes, a polycondensation reaction occurs between the isocyanate and the alcohol, but other secondary reactions can occur due to the high reactivity of the isocyanate. If there is water or humidity in the medium, the isocyanate group will react with it to form an amine and release CO2, the amine can react again with the diisocyanate to form urea. This reaction is used in the synthesis of PU for proper foaming, but in the synthesis of thermoplastic polyurethanes the water must be eliminated, since amines can be more reactive than alcohol and there can be simultaneous reactions competing with each other to form ureas.

3.4. Chain extenders

A low molecular weight (<400 g/mol) component is often added to PU synthesis that reacts with the free isocyanate groups to lengthen the chain of the material and increase its molecular weight. These can be classified into two: low molecular weight diols and short chain diamines; if a diol is used, new urethane groups will be formed, conversely, if an amine is used, urea groups will be formed. Without a chain extender, a PU formed by direct reaction between a macrodiol and a diisocyanate would have very poor physico-mechanical properties and would not exhibit phase segregation. (Prisacariu, 2011)

Generally, in the synthesis of thermoplastic polyurethanes, aliphatic diols are used as chain extenders, the most common being 1,4-butanediol (BD). Figure 15 shows the chemical structure of the 3 most commonly used chain extenders in PUR synthesis (Prisacariu, 2011).

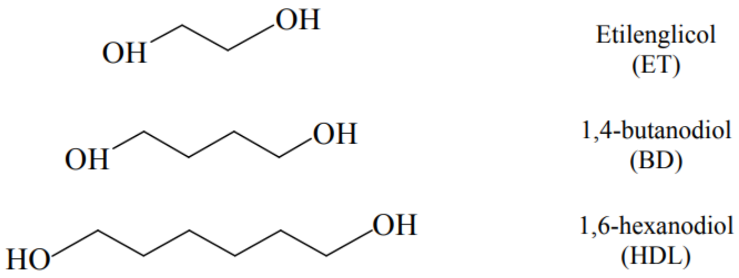


Figure 15 Chemical structure of chain extenders for PU synthesis.

3.5. Chemistry of PURs

The synthesis of PUR's is a polyaddition reaction between the hydroxyl group (-OH) of the polyol and the isocyanate group (-NCO).

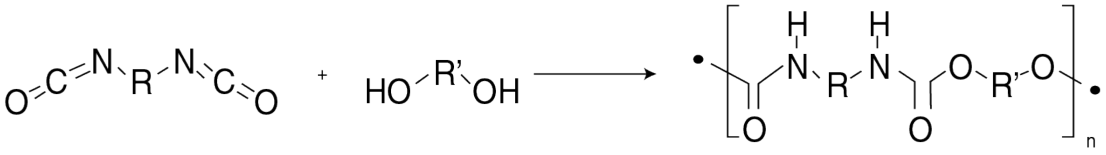


Figure 16 Synthesis of PUR's by polyaddition reaction.

PURs are polymers in which the main chain is composed of aliphatic or aromatic functional groups R1 and R2, linked together by urethane groups. Where R1 represents the aliphatic, aromatic or alicyclic radicals coming from the isocyanate monomer, and R2 is a more or less complex group derived from the diol or polyol component.

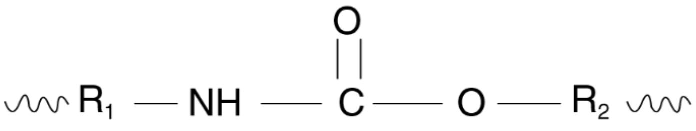


Figure 17 Molecular formula of PUR's

PUR is considered not very thermally stable mainly due to the existence of these urethane bonds, because degradation usually starts at the urethane bond at a temperature between 150 and 200 ºC. (Cooper, 2016)

3.5.1. Synthesis procedures of polyurethanes (Yang C F. L., 2018)

There are several methods for the synthesis of polyurethanes; the most common are classified according to: the medium in which the reaction takes place, the order of addition of the reagents, the number of process steps or the type of curing.

The synthesis can be carried out in organic solvents, in aqueous media or without the presence of solvent. One of the differences is that the solvent-free synthesis favors heat dissipation and must be compressed in a hydraulic press to form plates.

Depending on the order of addition of the reagents, polymerization can be carried out by the one-step method or the pre-polymer (two-step) method:

3.5.1.1. One-stage method

In this method, the formation and extension of the prepolymer occurs simultaneously, the polyol, diisocyanate, chain extender and a catalyst are mixed; it should be noted that the first three named components must be in the same proportion so that the reaction does not deviate and form undesired products. The advantages of this method are: its high reaction speed and that it does not require solvents, in addition, this method is used on an industrial scale since it does not require the reaction of the pre-polymer, reducing production costs, on the other hand, its disadvantage is its difficult control of the reaction.

3.5.1.2. Pre-polymer or two-stage method

In the first stage of this method, the macrodiol is added with the diisocyanate in excess, resulting in a pre-polymer with free isocyanate groups. In the second stage, the chain extender is added, which reacts with the excess isocyanate to give rise to the segmented polyurethane. The advantage of this method is that since it is a two-stage polymerization, there is a better control of the reaction, since the competitiveness between the macrodiol and the chain extender is avoided due to the difference in reactivity, in addition, there is an improvement in the mechanical properties of the product, since by this method the molecular weight distribution is narrower than when there is only one stage. One of its disadvantages is that due to the high mass of the segmented PUobtained, there is an unbalanced increase in the viscosity of the system. (Prisacariu, 2011) The viscosity of the PUis increased in an unbalanced way.

3.5.1.3. Morphology and properties of thermoset polyurethanes.

Polyurethanes can be characterized according to the structure they possess; they can be of fully bonded structure or of segmented structure. These types of structures will depend on the reagents used for their synthesis, taking into account properties such as: their chemical nature, proportion, affinity, reaction speed, molecular weight, among others. In addition, the morphology of polyurethanes may present a primary, secondary or tertiary structure which will be a cause of the properties mentioned above (Cooper, 2016).

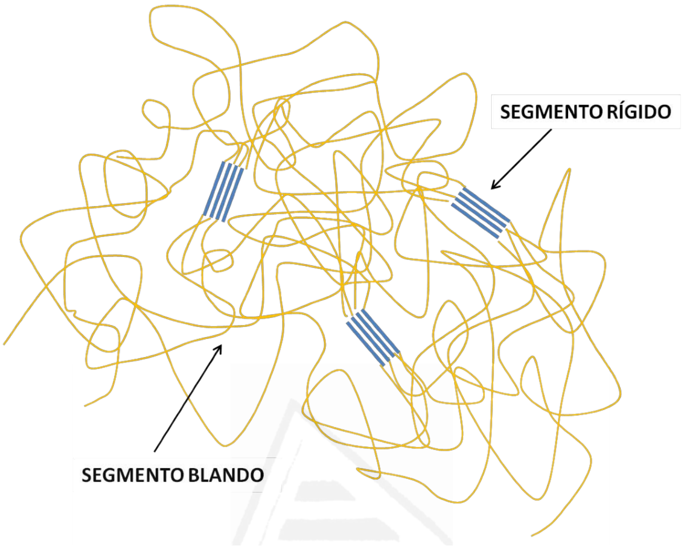


Figure 18 Segmented structure of a thermoplastic PU. (Council, 2015.)

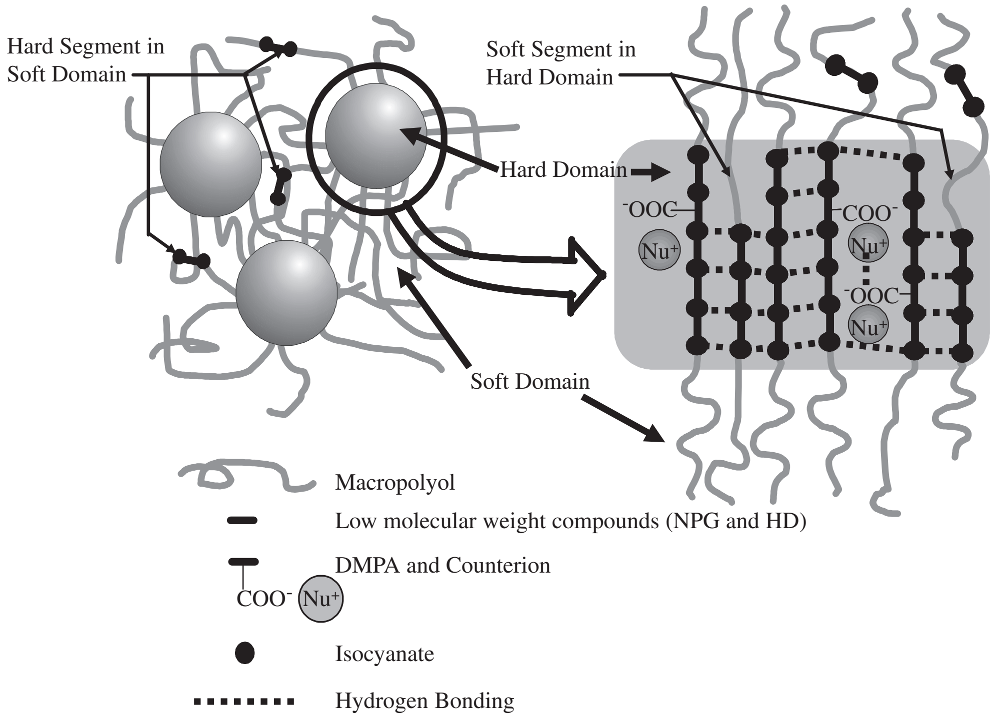


Figure 19 Schematic illustration of the microphase separation structure of a film produced from PUD. (Council, 2015.)

3.5.1.4. Morphology (Yang C F. L., 2015), (Li S. B., 2019)

Fully bonded structure polyurethanes are obtained from polyesters with high crystallinity, which will decrease the chain length, increase its hardness and crosslink density resulting in stiff and less elastomeric single-phase polyurethanes.

The segmented structure is a characteristic of thermoplastic polyurethanes considered block co-polymers that possess rigid parts and flexible parts having between them an alternating arrangement. The rigid segments are composed of isocyanates and chain extenders, these hardness properties are characteristic of the urethane groups and will be determinant of their mechanical properties, in addition, they possess polar behavior, high solubility and low molecular weight. On the other hand, the flexible segments are composed of macrodiol, these elasticity characteristics allow them to possess adhesive properties if they are a majority in their structure, in addition, they have apolar behavior, low solubility and high molecular weight. There is an incompatibility between the rigid segments and the flexible segments due to their chemical properties, therefore, a phase separation is generated in their structure. The rigid segment is linked to its neighboring chains by hydrogen bridges, while the flexible segment is wrapped around each other, this phase separation is responsible for giving the particular properties to the material.

In terms of the complexity of its arrangement, PU has a primary structure that occurs when the rigid and flexible segments are distributed. The secondary structure occurs in the formation of the hydrogen bridges of the rigid segment, causing the formation of areas with greater and lesser organization depending on the distance and location of the chains, since this bond is formed between the carbonyl groups (-C=O) and the urethane groups (-NH) present in the structure.

The tertiary structure is given by the separated morphology of the phases, where the parts rich in flexible segment wrap around each other and the parts rich in rigid segment are joined by hydrogen bonds, this crystalline structure will depend on the proportion between the isocyanate and the alcohol and the nature of the same. It must be taken into account that the phase separation is not total but partial, therefore it is necessary to define the starting reagents since it will be an important characteristic in the affinity of the same.

The rigid and flexible segments of a PU complement each other, since each one fulfills a very important function in its physical-mechanical properties, as its name indicates, the rigid segment provides hardness to the material while the flexible segment is characteristic of the elastomeric properties, on the other hand, the flexible fragments control the properties at low temperature conditions while the rigid ones at high temperatures. Consequently, depending on the amount of the type of segment they have, their properties will depend, for example, if the soft segments are in majority, the material will present high deformability, on the contrary, if it has more rigid segments this property will decrease, the melting points and the resistance to abrasion will increase.

Sometimes hydrogen bridge bonds can occur between the -NH and -C=O groups of the urethane groups of the rigid segment with those of the flexible segment. Some authors have established that in order to obtain good properties in PURs, phase segmentation must be present and that this miscibility is a negative factor for PURs. However, too much separation between the phases can represent fragility of the material.

3.5.1.5. *Structure-properties relationship*

The relationship between the structure of PU and its properties is determined by aspects such as: molecular weight, degree of polymerization, intermolecular forces or secondary bonds, rotational capacity of the polymer chains, crystallinity and morphology. Molecular weight affects properties such as melting point, elongation, glass transition temperature and elasticity when reaching a limiting value, on the contrary, aspects such as solubility and rigidity increase. (Li S. B., 2019)

Intermolecular forces or secondary bonds bind PU chains together and cause Young's modulus, maximum breaking strain, density, hardness, organic solvent swelling and glass transition temperature to increase, however, PU chains cannot be ordered if the forces are too high as the branching points reduce their mobility.

The rotation capacity of the polymeric chains is limited by the chemical groups that constitute them, the aromatic rings give hardness to the polymer, therefore, if the chemical structure of the PUR is formed mostly by this, the rotation will be affected, however, the PU can be formed by flexible groups such as the ether group. In addition, there are some properties that can increase the ease of rotation and decrease the glass transition temperature.

The ordering of the PU chains is decisive in the crystallization of the structure, this characteristic decreases the solubility, flexibility, elongation and increases the hardness, deformation strain and melting point.

The occurrence of flexible segments and rigid segments is also important in the properties of polyurethanes. The flexible segments give rise to ordered structures that generate interactions, which improve the thermal, viscoelastic and surface properties and increase the crystallinity of the sample. On the other hand, rigid segments affect the Young's modulus, rotational capacity and hardness of polyurethanes and decrease the molecular weight and crystallinity.

3.5.1.5.1. Impact of flexible segments on PU properties.

Phase separation increases with increasing chain length of the flexible segment and decreases with decreasing polarity. When there is an increase in the length of the soft segment there is a greater number of interactions and a more ordered structure is formed. On the other hand, the decrease in the polarity of the chains is due to the absence of functional groups of this type, which favors the absence of miscibility between the rigid and flexible phases.

Taking into account the macrodiols that can be used for the synthesis of polyurethanes, it is more favorable to use polyesterdiols or polycarbonatodiols if the aim is to increase the polarity of the flexible segment, which in turn increases the mechanical properties. (Li S. B., 2019)

3.5.1.5.2. Impact of rigid segments on PU properties.

The crosslinking points when the rigid chains are joined by hydrogen bonds form a compact structure and give the material crystallinity characteristics, these can be amorphous, para-crystalline or micro-crystalline.

By means of the diisocyanate/macroglycol molar ratio (NCO/OH) the amount of rigid segments in the PU is determined to a great extent, the higher this ratio, the lower its viscosity and the size of its chains, there will be an increase of rigid segments and less phase separation, that is to say, greater miscibility which improves the rheological properties of the material. On the other hand, if the ratio is lower, there is better thermal stability.

Isocyanate is a key reagent that defines the final properties of polyurethanes, since it determines the number of interactions between the chains, crystallinity, viscoelastic properties and adhesive properties. Polyurethanes present better mechanical properties if the isocyanate is aliphatic since due to its chemical structure it has a number of carbon atom pairs that have a higher melting point in the crystalline domains. (Li S. B., 2019) The isocyanate is a key reactant that defines the final properties of polyurethanes.

3.6. Vegetable Oil–Based PURigid Foam

As early as 1974, Lyon had already successfully prepared PUR foam from hydroxy methylated castor oil, safflower oil, and polyol esters of castor acids. (Lyon, Garrett, & Franker, 1974)

Research effort has been put into producing PU foams using soy-based polyols. In 2000, Guo and co-workers prepared HCFC- and pentane- blown PUR foams from soy-based polyols made from epoxidation followed by oxirane ring-opening. (Guo & Javni, Appl. Polym Sci, 2002) Nevertheless, these foams were found to have inferior mechanical and thermal insulating properties though higher thermal degradation temperature (measured by TGA) than foams made from petroleum-based polyols (see Table XXXX, foam C). The effect of catalysts, surfactant, water, cross-linker, blowing agent and isocyanate on the foam properties were also studied. It was found that TEGOSTAB® B-8404(Goldschmidt, polyether-modified polysiloxane), which was a general purpose surfactant for rigid foams, turned out to be more effective than other surfactants. The k value of the material, did not change significantly when the amount of surfactant was above 1.0 pph. The compressive strength increased with increasing amount of water while the k value stayed constant when the amount of water was above 2 pph. Three cross-linkers were tested: triethanolamine, trimethanolylpropane, and glycerin. Glycerin was found to be the best cross-linker and the foam shrank the least at 5-10 pph of glycerin.

Since then, more research has been done to understand the properties of soy-based PU foam. Guo et al. (Guo, Zhang, & Petrovic, Mater. Sci, 2006) continued to investigate the effect of soy-based polyol structure on the PUR foam (see Table 10, foam B). The polyols made from hydroformylation followed by hydrogenation were compared to those by epoxidization followed by methanolysis. The former type polyol, having primary hydroxyls, reacted faster and more completely than the latter one, which had secondary hydroxyls. The resulting polyurethanes from the latter type polyol had lower Tg. Since Tg is a measure of rigidity of plastics, foams from latter type polyol were less rigid. Unlike petroleum-based polyols, which were pure, soy polyols were mixtures due to the presence of different types of fatty acids in the soybean oil. Petrovic et al. (Petrovic, Guo, Javni, Cvetkovic, & Hong, 2008) had examined the effect of heterogeneity of the soy-based polyol structures on the foam properties. They found that this heterogeneity actually had no obvious effect on the mechanical properties of glassy PU(glassy polyurethanes had high modulus), but a negative effect on rubbery PU(rubbery polyurethanes had low elongation).

Narine et al. (Narine, Kong, & Bouzidi, 2007) prepared PUR foam using three polyols: soy-based polyol, canola oil-based polyol, and crude castor oil (see Table 10). The reactivity of canola oils-based polyol was found to be higher than that of both soy-based polyol and castor oil-based polyol. Importantly, they appeared to be the first to probe the dynamic mechanical properties of bio-based PUR foam.

Tu et al. (Tu, Kiatsimkul, Suppes, & Hsieh, 2016) prepared fifty natural oil-based polyols and replaced up to 50% of the petroleum-based polyol in water blown PUR foam to study their potential for replacement of the petroleum-based polyol. They characterized the OH number of the synthesized vegetable oil-based polyols and investigated the density, k value, and compressive strength of the foams. Though most of the foams had inferior properties compared to those made from 100% petroleum-based polyol, some foams made from 50% hydroxyl soybean oil, epoxidized soybean oil reacted with acetol, and oxidized epoxidized diglyceride of soybean oil can have relatively better k value and compressive strength.

Table 10 Comparisons of the formulations of PUR foams made from petroleum-based polyol and soy polyol.

Formulation	**Petroleum oil-based**	**Soybean oil-based**
	Control	
Polyol (parts)	100	100
Polyol OH number	450-500	212
Gelation Catalyst (parts)	0.5	1.0
Blowing Catalyst (parts)	2.1	1.0
Surfactant (parts)	2.5	2.0
Physical blowing agent (parts)	9.6 (n-pentane)	11-14 (HCFC)
Glycerin (parts)	--	29
DI water (parts)	1.9	2.0
MDI index	110 (polymeric)	120 (crude)

(Chang, Xue, & Hsieh, 2001)

Comparing the formulations of the PUR foams between the petroleum-based and soy-based, the amount of the catalysts, surfactant, water, and isocyanate index was close but the amount of physical blowing agent and glycerin varies. The biggest difference came from the OH number of the polyol. Petroleum-based polyol had a much higher OH number at 450-500 than that of the soy-based polyol, which was about 200. This turned out to be an important issue and will be discussed further. Soy-based PUR foams had comparable density with that of petroleum-based PUR foams (except B). Foam A and D seemed to have good compressive strength. Nevertheless, the fact was that foam A was made from a polyol blend of 50% soy polyol and 50% petroleum-based polyol, and the measured compressive strength values had a big error bar as well. Foam D had much higher density, which made it stiffer. Very few studies on soy-based PUR foam had reported the closed cell content, the only reported measured value was about 9%, which was extremely low. (Guo, Zhang, & Petrovic, Mater. Sci, 2006) And in this study, the Tg of the soy-based PUR foam was found to be lower than the typical maximum usage temperature of the commercial petroleum-based PU foam. Thermal insulation property is a very important property for the PUR foam. Foams made from substituting 50% petroleum-based polyol with soy polyol had a wider range and about 10% higher k value than the petroleum-based foam. Foams made from solely soy polyol also had at least 10% higher.

In summary, some work has been done on developing soy-based PUR foams. Though they had comparable density to petroleum-based foams, their k value and compressive strength were inferior to the commercial products to different extents. A systematic and complete study on PUR foams from soy polyol is needed to fully understand the potential limitation of soy polyol in producing PUR foams. The goal of my research is to formulate PUR foam from soy-based polyols, characterize and compare foam properties with those from petrol-based foams, and then study the mechanism behind the property deficiencies and develop strategies to improve them. (Tu, Kiatsimkul, Suppes, & Hsieh, 2016)

3.7. Applications of PURs

The presence of the urethane group in their structure is the main characteristic of these polymers, which can be developed with very diverse physicochemical properties (Yang C F. L., 2015). For this reason, polyurethanes are formulated for a wide range of applications, including adhesives, elastomers, composites or foams, as shown in Figure 20.

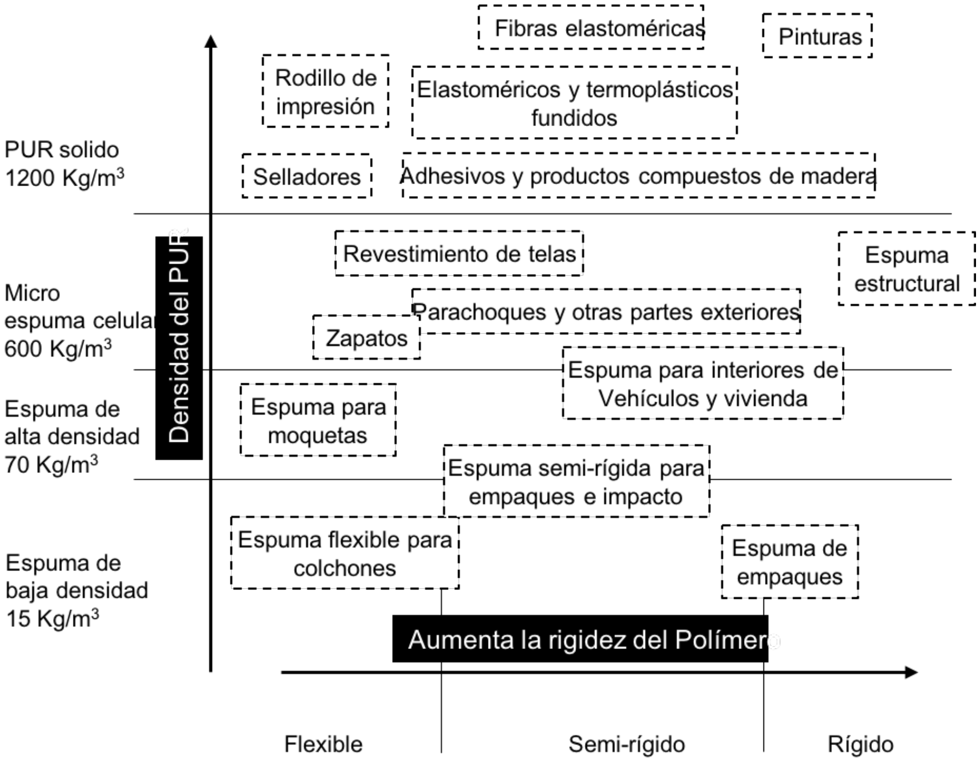


Figure 20 Different applications depending on the density and stiffness of PURs.

Figure 21 below shows the percentage participation of different industrial sectors in the applications that have been given to PURs at the international level, which is not the case in Colombia due to the costs associated with the production of PURs from petrochemical sources.

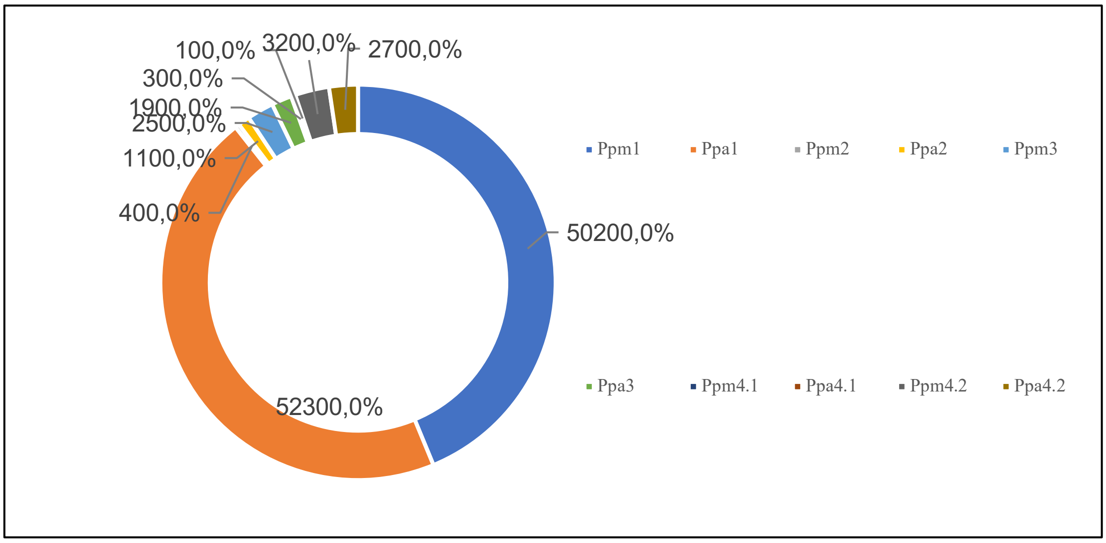


Figure 21 PU applications PUR´s

3.7.1. Building and construction

About 30 - 40% of the world's energy is consumed by the building sector, which is responsible for one third of greenhouse gas emissions. Being an excellent material as a thermal insulator, PUR rigid foam has been widely used in the field of building envelope insulation to save energy due to its low thermal conductivity, superior specific mechanical properties, and low density. [26] The building sector represents an important market for PUR foam.

The construction sector represents a market for a diversified portfolio of PU products. One of the largest applications is the use of PUR rigid foam as wall and roof insulation, insulation boards and void fillers for the space around doors and windows. Rigid foam adhesives are used in some window and door installations and in prefabricated housing. There are many benefits to using PUR rigid foams as insulation, such as energy efficiency, high performance, versatility, thermal/mechanical performance and environmental savings.

PUR foams have one of the highest U-values (heat transfer coefficient) among all commercial products available today. With typical values ranging from U 3.6 kcal-m-2-h-1-°C-1 to U 7.2 kcal-m-2-h-1-°C-1 per inch, thinner walls and lower profile ceilings are possible, maximizing efficiency, increasing space utilization and reducing operating costs for heating and cooling.

PUR rigid foams are manufactured with a low-density, slightly resilient, lightweight structure that is both dimensionally stable and moisture resistant with low vapor transmission. This special combination of properties allows manufacturers to design insulating products that are self-supporting and can be combined with a wide range of substrates without the need for additional adhesive and when combined with the right materials, function as external barriers against weather and moisture.

Some rigid PUR foams can be applied in situ to seal gaps and cover irregular shapes. These include spray foams, poured-in-place and single-component foams. PUR spray foams form a transparent layer of insulation, fill gaps and seams during application and cover irregular shapes that are difficult to insulate with rigid boards. This significantly reduces drafts while creating quieter buildings.

The qualities of PUR rigid foam are determined by reducing energy transfer, resisting moisture, maintaining dimensional stability, being airtight and often playing a structural role, they also perform well in extreme temperatures and resist moisture damage that can result from ambient condensation.

3.8. Social interest housing

Before understanding what social interest housing in Colombia is, it is important to know the country's situation. The actual government has as a goal to reduce by a 5.5% the housing deficit in the country, going from 12.6% to 5.6% in the last couple of years.

In addition, they were destined more than 2'085,714€ in subsidies so more Colombians can fulfil the dream of having a house on their own. The regions that receive more subsidies are Atlántico, Antioquia, Valle del Cauca, Magdalena, Córdoba, Cesar, Norte de Santander, Bolívar, Nariño, Sucre, Chocó and Cundinamarca. These investments not only gave a house to those in need but also generated 300.000 new jobs.

According to the national government (article 91 de la ley 388 de 1997), the social interest houses are those developed to guarantee the right of having a house to the families with the lowest income. In every Development National Plan (Plan Nacional de Desarrollo) the national government will stablish the type and peak price of the destined solutions for the families, taking into account the habitational shortfall, the credit access possibilities, the offer possibilities, the credit resources amount for the financial sector and the state's sum of funds destined to the housing programs.

Nonetheless, the destined resources in money or any kind by the national government, in legal obligations to promote the social interest housing, will be conducted primarily to attend the poorest population of the country, according to the unsatisfied basic needs indicators and the results of the incomes and outcomes studies.

In the government (Juan Manuel Santos 2014 – 2018), the value of the social interest house in Colombia must not exceed the sum of one hundred and thirty-five (135) legal valid minimum monthly salaries. This year the legal valid minimum monthly salary is $781.242 COP, this means more or less 232 €.

Chapter 4: Case Study: Costing of PUR's for VIS

PUR's are thermosetting polymers widely used in modern life, within the applications currently being explored are those of housing constructions, where the material can generate an interesting competitive advantage over concrete, given its lighter weight characteristics, which determine transportation costs, on-site processing - foaming, and joints - which generates another competitive advantage of the material to meet specific design requirements and needing an environmental advantage as a determining variable to consider the material as a replacement in low-income housing, where cost is the main determinant, but the impact on the environment is a decisive factor in new architectural projects.

In this chapter the traditional costing of a VIS in Colombia is developed and the replacement in such costing will be made using palm oil PUR as replacement material in the housing structure to understand its differences. For the realization of this costing, it is taken as a basis what has been developed in the 2765146 a, us 20140309322 a1, wo/2013/050854, 11201401245s a1patents and its experimental results presented to obtain said property registration.

4.1. PUR's obtained from the registered process (patents)

4.1.1. Obtaining polyols from natural oils

Table 29 shows the #OHs for each palm oil in each of the routes used for the synthesis according to the patent routes.

Table 11 Characterization results of polyols by #OH (mg KOH/sample)

Routes	Source of polyol	Polyols	# OH (mg KOH / g $_{sample}$)

Route 1: Glycerolysis	Palmiste	Ppm1	502
	Palm	Ppa1	523
Route 2: Transesterification with pentaerythritol	Palmiste	Ppm2	4
	Palm	Ppa2	11
Route 3: Epoxidation of fatty acid methyl esters	Palmiste	Ppm3	25
	Palm	Ppa3	19
Route 4: Maleinised monoglycerides Method 1	Palmiste	Ppm4.1	3
	Palm	Ppa4.1	1
Route 4: Maleinised monoglycerides Method 2	Palmiste	Ppm4.2	32
	Palm	Ppa4.2	27
Route 5: Fisher Transterification	Palmiste	Ppm5	235
	Palm	Ppa5	240
Route 6: Epoxidation and glycerolysis	Palmiste	Ppm6	244
	Palm	Ppa6	240

* In yellow the polyols that were selected for the production of PURs.

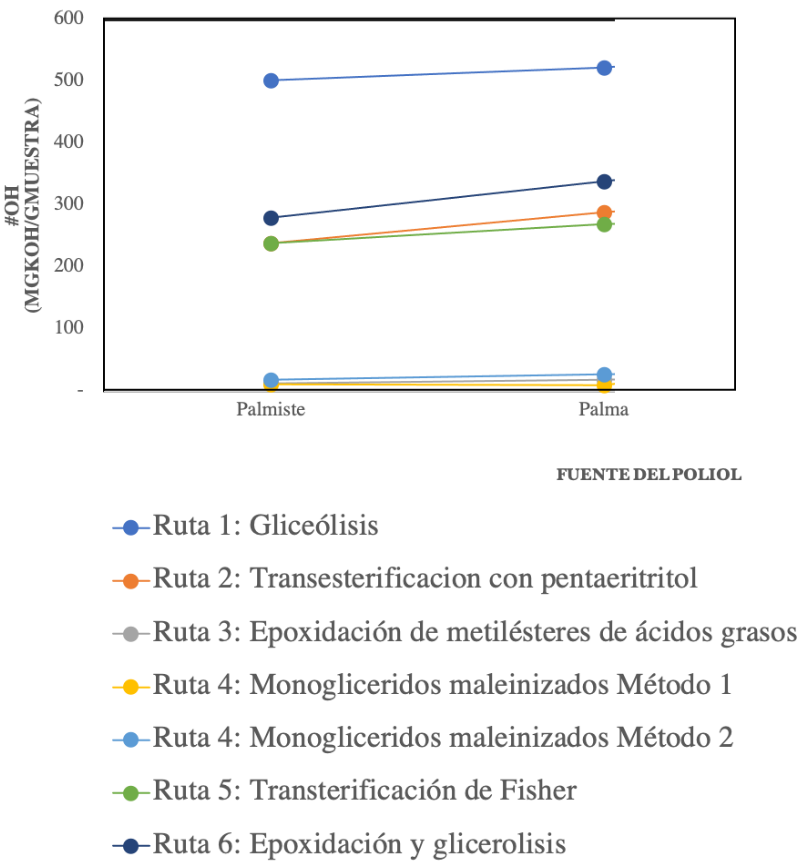


Figure 22 Number of OH of the polyols obtained.

It can be seen that Route 1 and Route 2 give the highest #OH values. Routes 5 and 6 give similar and slightly lower values than Routes 1 and 2. The remaining Routes: 3, 4.1 and 4.2, give very low values, which are quite negligible for this comparative and costing.

On the other hand, Route 1 is the simplest and this indicates a more economical structure. Routes 5 and 6 would be expected to give higher #OH, but surely sorbitol has greater steric hindrance when reacting its OH groups with sodium hydroxide, which would explain the lower #OH value compared to that of glycerol. In the case of Route 6, it is a more complex route than Route 1, and, therefore, although OH groups are obtained from the double bonds of unsaturated fatty acids, the low yield makes the result worse.

The hydroxyl values obtained by route 1, presented high hydroxyl values and, taking into account the values that are required, as a minimum, to obtain PUR's [23] in their application in construction, these values are optimal, and allow using these polyols in the preparation of PU rigid foams.

4.1.2. Synthesis of PURs from vegetable oils

Table 13 shows the PURs obtained with different mixtures of precursors and routes defined by the patents and which were used to select the one with the best structural performance for the calculation of the VIS-type housing.

Table 12 Summary of selected PUR's

Route and Precursors	PU	Compression	Shear	Tension	Image of sample
Route 1 MDI + Ppm1	PU01	3,45	3,34	4,85	
Route 1 MDI + Pa1	PU02	3,45	3,35	4,20	
Route 2 MDI + Ppm1	PU03	3,26	3,187	4,96	
Route 2 MDI + Pa1	PU04	3,22	3,192	4,97	

Route 3 MDI + Ppm1	PU05	3,45	3,707	4,98	
Route 3 MDI + Pa1	PU06	3,31	3,699	4,43	

PUR commercial (reference)	4,56	4,3	4,36	

In Table 39, the PURs present a visual difference that seems to show that a better distribution of the PU05 cells compensates for a greater compaction of the material and gives a better mechanical performance, and even visually and in compaction it is similar to the commercial PUR.

From the results obtained for the mechanical tests of tension, compression and shear of the synthesized PURs, it can be evidenced that the values obtained by route 3 using palm kernel yields a PU05 with better mechanical values with values closer to the commercial PUR, being this the one used for the cost comparison.

4.2. Costing of a traditional VIS in Colombia

4.2.1. Costing of a PUR board

The costs of a PUR board obtained from natural sources are given not by an industrial scaling but by a prototype approximation, calculated with the following equation:

$$C = (cR * vR) + (cE * vE) + (cF + cV).$$

Equation 1 Cost calculation of PUR boards.

Where:

C: Cost of the board
cR: Quantity of reagent used
vR: Cost of reagents
cE: Equipment usage time
vR: Cost of use of the equipment
cF: Fixed costs associated with the synthesis process
cV: Variable costs associated with the synthesis process.

Resulting in the values shown in Table 40.

Table 13 Costs per board of the selected PURs.

PUR	Board Cost (2x2.5x0.2)m ($)
PU01	$135.000
PU02	$155.000
PU03	$169.000
PU04	$160.000
PU05	$160.000
PU06	$160.000
PUR Commercial	$194.000

In Table 39 we observe that PU05, which has the best mechanical performance, has a somewhat lower price than commercial P. Therefore, this PUR is a good competitor to commercial PUR

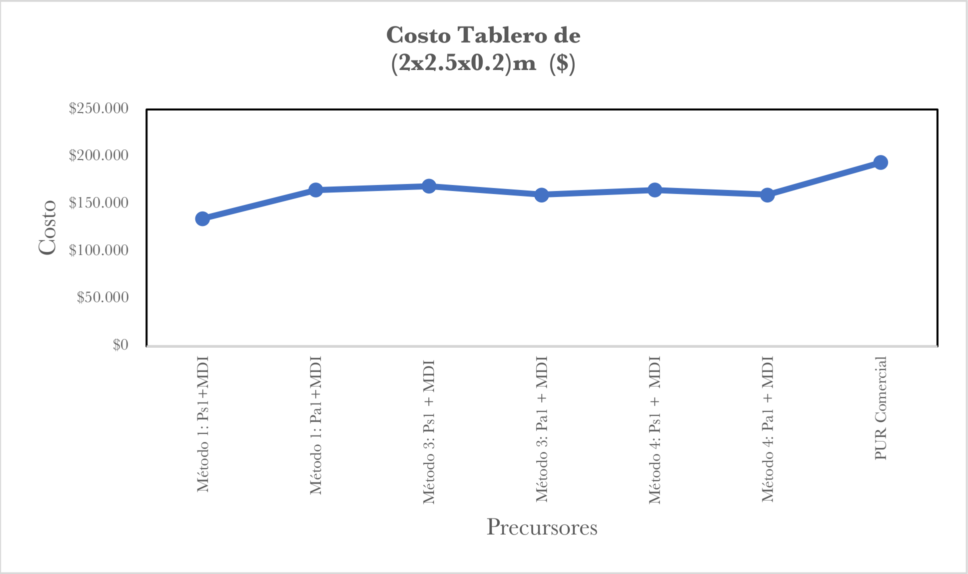


Figure 23 Comparison of board costs of the PURs obtained (2 x 2.5 x 0.2) m

Figure 60 shows that the PUR's obtained from the patent have prototype costs very similar to the reference or commercial PU's, which makes them an interesting alternative.

4.3. Costing of a social housing

The basic requirements for a VIS type housing that responds to distribution, Bioclimatic: passive techniques and sustainability, are shown in Figure 24:

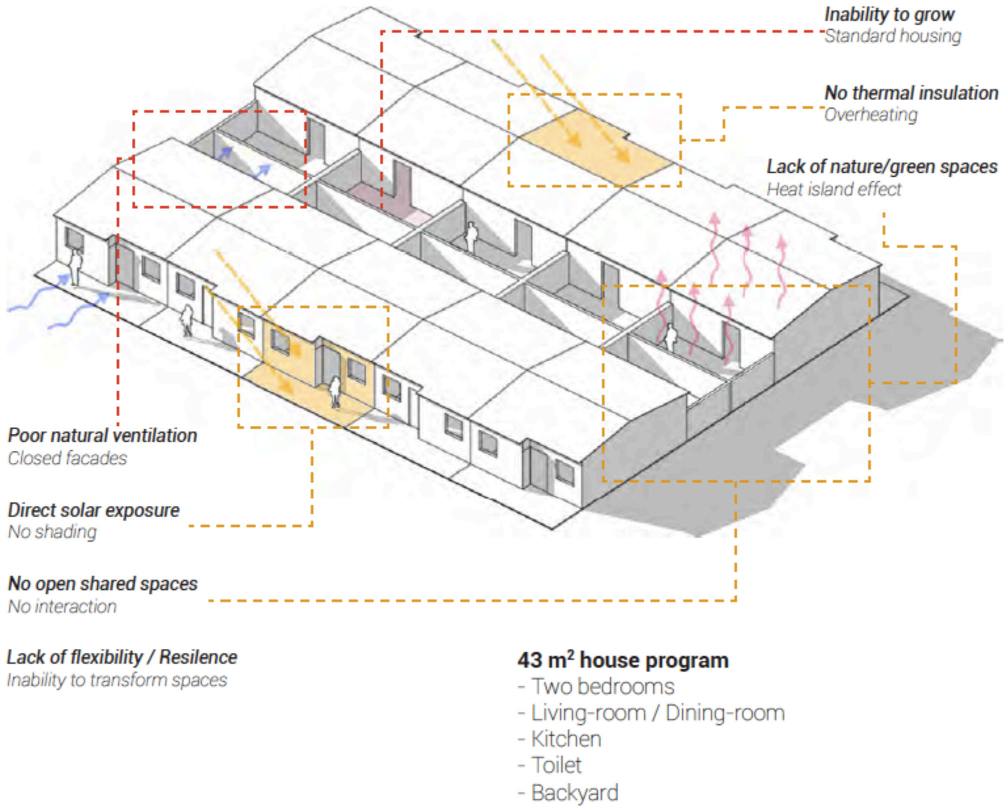


Figure 24 Requirements for a VIS type housing

4.3.1. Construction costs

The valuation of a VIS type housing, determined according to the Colombian policy, was made with the following equation:

$$VIS = M + I$$

Equation 2 Calculation of VIS costs

Where:

VIS: Cost of a social interest housing.
M: cost of materials
I: installation cost

43 m2 house program

- Two bedrooms
- Living-room / Dining-room
- Kitchen
- Toilet
- Backyard

Table 14 Costs obtained for the traditional method of VIS type housing

Item	Cost
Preliminary works	€ 153,97
Foundations	€ 1.839,75
Structure	€ 331,41
Concrete walls	€ 697,24
Concrete roof	€ 1.286,43
Wooden carpentry	€ 249,17
Metallic carpentry	€ 379,00
Finishes	€ 1.861,94
Sewage water treatment system	€ 223,07
Onsite training	€ 157,14
Total direct costs	€ 7.179,12

The above direct costs correspond to a VIS where the walls and roof are made of concrete.

4.4. Costing of a VIS type housing with PUR

Table 15 Costs obtained for the traditional method for a VIS type housing.

Item	Cost
Preliminary works	€ 153,97
Foundations	€ 1.839,75

Structure	€ 331,41
Concrete Walls	€ 127,45
Concrete Roof	€ 522,34
Wooden carpentry	€ 249,17
Metallic carpentry	€ 379,00
Finishes	€ 1.861,94
Sewage water treatment system	€ 223,07
Onsite training	€ 52,30
Total direct costs	€ 5.740,40

The savings generated by building a house with these new materials, compared to the cost of a house made with concrete, have been calculated and compared with the synthesis performance of the new materials. The savings, in general, are between 18 and 20%, generating a very effective possibility of replacing the material in a construction sector that wants to differentiate itself from the economic factor and sustainability in architecture.

4.5. Prospective of the VIS in Colombia

We can rely on many aspects to explain the demand for low-income housing in Colombia, from the civil war of more than fifty years that has caused forced displacement, to corruption, poverty, bad economic models, etc. In this work, what is conceived as a problem is the construction of housing itself, its architecture, its urban planning, its ease of construction from the search for alternative materials that propose ways to close the gaps.

The roof, walls, windows and doors are fundamental elements to generate large-scale construction of the housing that the country needs, and it is there where the cost of PUR sheets as a structural material justifies its participation in one of the territories with the largest African palm cultivation.

We cannot underestimate the work of the government with the National Planning Department and private partners such as the Adaptation Fund that are developing these houses, which on some occasions have done a very good job, but we can support initiatives with materials such as PUR that guarantee the creation of social housing with a lower environmental impact.

Chapter 5: Considerations

In this Thesis it has been shown that the polyols synthesized from palm and palm kernel oils are in most cases efficient raw materials for the preparation of PUR's and allow to guarantee basic mechanical properties for the application in VIS.

5.1. Conclusions

It is concluded that PUR foams are synthesized from polyols containing a #OH greater than 200 mg KOH/g, i.e., routes 1, 2, 5 and 6 are optimal for synthesizing polyols required as raw material for these. On the other hand, flexible PU foams must contain from 28 to 56 mg KOH/g, so method 2 of route 4 produces polyols containing this range of hydroxyl numbers.

Palm and palm kernel oils, through routes of epoxidation of fatty acid methyl esters and maleinization of monoglycerides are good precursors for obtaining flexible foams. This is explained by the structure of these two oils, which are mainly composed of saturated fatty acids (lauric acid and palmitic acid) and in a lower percentage of unsaturated fatty acids. Palm oil has approximately 40% oleic acid (monounsaturated) and only 10% polyunsaturated fatty acids, while palm kernel oil has 15% oleic acid and only 2.5% polyunsaturated fatty acids. Additionally, the maleinization of oils is an esterification and crosslinking reaction used to decrease #OH's and increase molecular weight, conditions expected in obtaining flexible foams.

It is evident that PUR occupies a large percentage of the market and has a great variety of utilities, therefore, an analysis has been made to determine optimal ways of synthesis of this material from biodegradable components such as vegetable oils, since the production of this material has been made from petroleum derivatives that present a great environmental problem due to the negative impact it has. For this reason, synthesizing the material with natural components presents an advance for the industrial sector that is opting to generate cleaner production alternatives and environmental sustainability, in addition, a decrease in the costs of raw materials that can meet the same characteristics of the traditional PU will be noticed due to the use of large-scale inputs in local production.

Regarding the physicochemical properties of PU, it can be concluded that this material presents great versatility linked to the raw materials used for its synthesis, since depending on its nature and proportion, the desired morphology of the final product will be obtained, which is why PU has been used in various presentations on an industrial scale, but posing a current challenge to the mechanical improvements versus the cost structure of the material.

It is possible to synthesize PU's, with mechanical properties similar to the commercial ones for competitive commercial applications. It was evidenced that with mechanical properties similar to PUR of petrochemical origin, the replacement of concrete for the manufacture of VIS in Colombia is an environmental alternative of great impact. When evaluating the cost structure of the selected PURs, it is clear that they compete with an advantage over concrete, which represents a novel alternative for SIVs.

5.2. Future work

Obtaining PUR foams from natural sources such as natural oils is a promising field. Since the aim is to obtain rigid PUR foams, it can be concluded that palm kernel oil had the best performance. Palm oil is one of the most produced crops in Colombia, so it would be a potential raw material that is found in abundance in the territory and at an economic price, thus reducing the production costs of these foams, for a competitive advantage over those originated from petrochemicals.

In the market, rigid PURs, due to their mechanical and thermal properties, are usually used as thermal and acoustic insulation panels in the construction sector. The study of the possible application of the rigid PUR's obtained in this research as insulating materials is in progress and the possibility of generating structural panels for low-cost housing opens a panorama in architecture to explore the possibilities of the material, henceforth it is proposed the reinforcement of PURs with waste fibers from the same agro-industry.

Given the original application of these materials according to the objectives of the thesis, it can be predicted that in future works the material will be validated in transportation applications both in the air and space industry.

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Appendix 1 Patents

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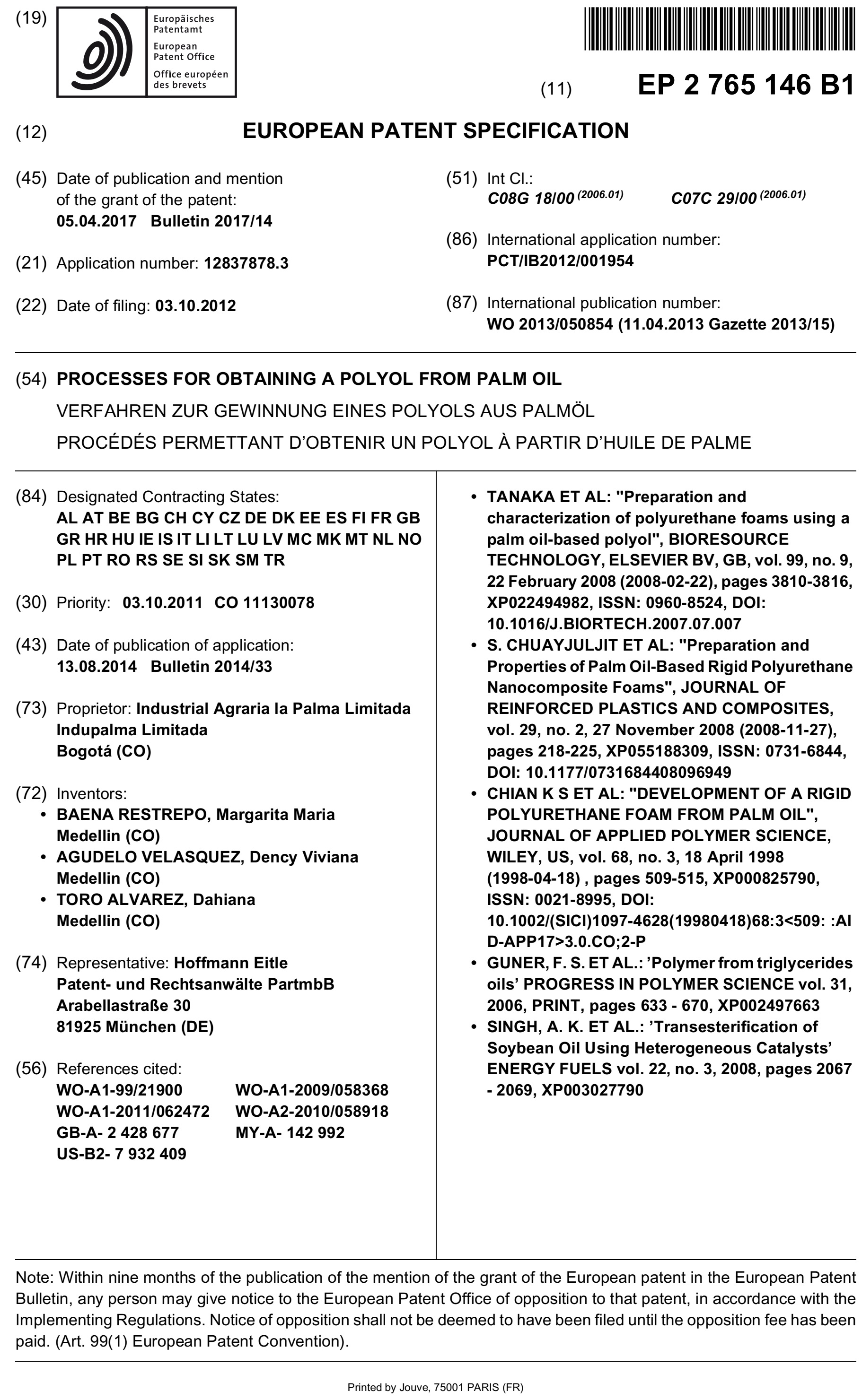

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(54) **PROCESSES FOR OBTAINING A POLYOL FROM PALM OIL**
VERFAHREN ZUR GEWINNUNG EINES POLYOLS AUS PALMÖL
PROCÉDÉS PERMETTANT D'OBTENIR UN POLYOL À PARTIR D'HUILE DE PALME

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(54) # PROCESSES FOR OBTAINING A POLYOL FROM PALM OIL, POLYOLS OBTAINED FROM SAID PROCESSES, PRODUCTS DERIVED FROM SAID POLYOL AND METHOD FOR PREPARING SAME

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(57) **ABSTRACT**

The present invention relates to the process for production of a polyol from palm oil and of rigid polyurethane foams prepared from said polyol derived from palm oil. On the one hand, this invention provides a method for obtaining monomeric polyols from palm oil that have hydroxyl number between 50 450 mgKOH/g sample. The polyols of the present application may be obtained by means of a procedure based on the following four mother routes: Route 1: maleinisation of the fatty acids of palm oil; Route 2: glycerolysis of palm oil; Route 3: trancesterification of palm oil; and Route 4: epoxidation of unsaturated carbon-carbon links of palm oil. Additionally, other modalities of the invention permit obtaining polyols from the combination of these mother routes. In other realizations of the invention polyurethanes are prepared from polyols obtained through any of the four routes or by combinations of the same. In a mode of the invention the polyurethanes are produced through the reaction of a mixture of a polyol obtained through the present invention, a commercial polyol, a surfactant, a catalyst and an isocyanate. The polyurethanes may be foams of rigid high density polyurethane.

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Declaraciones según la Regla 4.17:

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- *sobre el derecho del solicitante a reivindicar la prioridad de la solicitud anterior (Regla 4.17(iii))*

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(54) Title: PROCESSES FOR OBTAINING A POLYOL FROM PALM OIL, POLYOLS OBTAINED FROM SAID PROCESSES, PRODUCTS DERIVED FROM SAID POLYOL AND METHOD FOR PREPARING SAME

(54) Título : PROCESOS PARA LA OBTENCIÓN DE UN POLIOL A PARTIR DE ACEITE DE PALMA, POLIOLES OBTENIDOS A PARTIR DE DICHOS PROCESOS, PRODUCTOS DERIVADOS DE DICHO POLIOL Y SU MÉTODO DE PREPARACIÓN

(57) Abstract: The present invention relates to a process for producing a polyol from palm oil and to rigid polyurethane foams prepared using said polyol derived from palm oil. On the one hand, the present invention provides a method for obtaining monomeric polyols obtained from palm oil, which have a hydroxyl number between 50 and 450 mg KOH/g of sample. The polyols of the present application can be obtained by a procedure based on the foliowing four mother routes: route 1: maleinisation of the fatty acids from the palm oil; route 2: glycerolysis of the palm oil; route 3: transesterification of the palm oil; and route 4: epoxidation of the unsaturated carbon-carbon bonds of the palm oil. In addition, other embodiments of the invention make it possible to obtain polyols from the combination of said mother routes. According to another aspect of the invention, polyurethanes are prepared using the polyols obtained via any of the four routes or via a combination thereof. In one embodiment of the invention, the polyurethanes are produced by reacting a mixture of a polyol obtained in accordance with the present invention, a commercially available polyol, a surfactant, a catalyst and an isocyanate. The polyurethanes can be high-density rigid polyurethane foams.

(57) Resumen: La presente invención se relaciona con el proceso para, la producción de un poliol a partir de aceite de palma y con espumas de poliuretano rígido preparadas a partir de dicho poliol derivado de aceite de palma. De un lado, la presente invención proporciona un método para la obtención de polioles monoméricos obtenidos a partir de aceite de palma y que tienen número de hidroxilo entre 50 y 450 mgKOH/g muestra. Los polioles de la presente solicitud pueden ser obtenidos por medio de un procedimiento basado en las siguientes cuatro rutas madre: Ruta 1: maleinización de los ácidos grasos del aceite de palma; Ruta 2: glicerólisis del aceite de palma; Ruta 3: transesterificación del aceite de palma y Ruta 4: epoxidación de los enlaces insaturados carbono- carbono del aceite de palma. Adicionalmente, otras modalidades de la invención permiten la obtención de polioles a partir de la combinación de estas rutas madre. En otro aspecto de la invención se preparan poliuretanos a partir de los polioles obtenidos mediante alguna de las cuatro rutas o mediante la combinación de las mismas. En una modalidad

[Continúa en la página siguiente]

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Description

FIELD OF THE INVENTION

[0001] Synthetic polymers were invented about 60 years ago and from then on much progress has been achieved in the field of their applications. Polyurethane is a polymer obtained through condensation of polyols combined with polyisocyanates. It is subdivided into two major groups: thermostables and thermoplastics. The more usual thermostable polyurethanes are foams frequently used as thermal insulators and as resilient foams, but there are also polyurethanes that are high performance elastomers, adhesives and sealants, paints, fibers, packaging sealants, joints, preservatives, automobile components, elements in the construction industry, furniture industry, and other multiple applications.

[0002] Polyols used in the production of polyurethanes are generally compounds with molecular weight in the range of 500 to 5000 g/mol. Depending of the length of the chain of these diols and glycols, the properties of the polyurethanes change. If the polyol has a low molecular weight, it makes rigid plastics, and if it has a high molecular weight it produces flexible elastomers. Polyols are reactive substances, usually liquids, which contain at least two groups that react to isocyanate linked to one molecule. They have a deep effect in the properties of finished polyurethane. The properties of the polymers are associated with the links to isocyanate, but the structure of polyol exercises a direct action on the processing and finishing properties of the polymer.

BACKGROUND OF THE INVENTION

[0003] The polyols used in the polyurethane production industry are generally derived from petroleum, but currently there is a trend to use renewable sources such as vegetable oils for production of polyols based on these oils.

[0004] The production of polyols from vegetable oils has been described in several documents in the state of the art:

> Patent Application U.S. 20070232816 reveals a process for the production of a polyol monomer which consists of reacting an unsaturated fatty acid or its corresponding triglycerides with a polyhydric alcohol in the presence of a catalyst and an emulsifier in order to prepare a monoglyceride. Said process also comprises an epoxidation stage of the unsaturated fatty acids of said monoglyceride, and a reaction stage of the epoxidized monoglyceride with a polyhydric alcohol.

[0005] Publication WO/2006/012344 provides methods for the preparation of unsaturated polyols based on modified vegetable oils, as well as methods for the production of oligomeric polyols based on modified vegetable oils. This publication shows a method of manufacturing an oligomeric polyol based on a modified vegetable oil, where a mixture is made to react that comprises an epoxidized vegetable oil and a compound that allows the opening of the ring for forming an oligomeric polyol based on the modified vegetable oil, where the oligomeric polyol based on the modified vegetable oil comprises at least 20% of oligomers and has a viscosity at 25°C of less than approximately 8 Pa s.

[0006] Publication WO/2009/058367 as well as Publication WO/2009/058368 refer to methods for obtaining a polyester polyol from natural oils. Such methods comprise the stage of reacting the monohydric fatty acids to the esters with a multifunctional reagent initiator to form the polyester polyol. This document reveals a process where a methanolysis of oils (Sunflower, Soya, Canola) is performed followed by an epoxidation process.

[0007] Patent Application U.S. 6,433,121 reveals a method for the production of polyols based on natural oils through the use of a two consecutive-stage process involving epoxidation and hydroxylation. This document mentions in a general manner that palm oil may be used; however, without limitation, the preferred realization of the invention corresponds to the use of soybean oil.

[0008] Publication WO/2009/058368 reveals methods for obtaining a polyester polyol from natural oils. Said method comprises a stage of reacting the hydroxylated fatty acids to the esters with a reagent multifunctional initiator to form polyester polyol. The process revealed in this document performs a methanolysis of oils (Sunflower, Soya, Canola) followed by a process of epoxidation. Additionally, the document mentions in a general way that palm oil could be employed in the process.

[0009] In the research published in the Article by G. Ruiz Aviles, "Obtaining and characterizing of a biodegradable polymer from Cassava starch," Engineering and Science, Medellin, 2006, a biodegradable polymer is obtained from yucca starch by processing modified starch mixtures with glycerin and water as plasticizers, using an open mill and a single extruder spindle. The variables to control during the extrusion are: temperature, torque and spindle rotation speed profile. The polymer obtained has applications in food packaging and for garbage bags.

[0010] On the other hand, the article by H. Yeganeh. P. et al., "Preparation and properties of novel biodegradable polyurethane networks based on castor oil and poly(ethylene glycol)," Polymer Degradation and Stability 92, Iran, 2007, reveals a method of preparation of polyurethane with polyols obtained from castor oil and mixtures with polyethylene glycol that were synthesized through the reaction of the prepolymer with 1,6 hexamethylene diisocyanate. The polymer obtained has a rate of biodegradability compatible for use in biomedical applications.

[0011] The article by S. Ahmad, Md, et al., "Urethane modified boron filled polyesteramide: a novel anti-microbial polymer from a sustainable resource," European Polymer Journal, 2004, describes a procedure for obtaining an anti-microbial polymer from soybean oil; the polymer is composed of polyesteramide filled with boron that is polymerized to form a polyester amide urethane. The material obtained was evaluated for antimicrobial and antifungal activity, verifying that the different compositions inhibit microbial growth.

[0012] Another article, by V. Sharma, et al., "Addition polymers from natural oils: A review," Prog Polym. Sci. 31, India, summarizes the theoretical aspects of the production of polymers from renewable sources, especially from vegetable oils, showing the differences in the structure of each oil and its influence on the polymer properties. It poses various alternatives for natural oils such as soy, corn, tung, linseed, castor oil, plant and fish oil for the production of polymer materials.

[0013] Finally, the article by G. Gunduzb, et al., "Water-borne and air-drying oil-based resins," Progress in Organic Coatings 49, Turkey 2003, presents a procedure for the preparation of polyurethane dispersed in water for application as a varnish. The resin is produced by preparing a maleinised monoglyceride, TDI as isocyanate, silicone, and ethylene diamine. Sunflower oil was used for this development as a renewable resource to produce the monoglycerides.

[0014] Palm oil is the second most cultivated vegetable oil in the world following soybean oil. Ninety percent of palm oil produced is exported from Malaysia and Indonesia. Palm oil is derived from the fruit clusters of the palm, is semisolid at ambient temperature due to the combination of triglycerides of high and low fusion points, and has a red-orange color due to its high content of carotenes. It is composed mainly of fatty acids, the amounts typical of these acids being: 45% palmitic, 40% oleic, 10% linoleic and 5% stearic. Thanks to its good resistance to oxidation and to heating at high temperatures, palm oil is employed in diverse industries for its good performance and economy. In energetic terms palm oil requires less energy for the production of one ton than other oils, such as soy and rapeseed oils.

[0015] Initially, palm oil production was only used for human consumption, but in view of the overproduction of palm oil in Malaysia, Thailand and Indonesia, the need to search for alternative uses for the oil has been identified. Some different areas of knowledge have been identified for its use, such as medicine, agriculture, development of new materials, civil works, and biofuels, among others.

[0016] The production of polyols from palm oil, specifically oligomeric polyols, has been described in Publication WO/2007/123637, which discloses oligomeric polyols obtained from palm oil and compositions that comprise these polyols, as well as a process for obtaining an oligomeric polyol based on modified palm oil, which comprises providing an epoxidized composition based on palm oil and making it react with a compound that allows the opening of the ring to form an oligomeric polyol where the oligomeric polyol based on the modified palm oil comprises at least 40% oligomers by weight, has a hydroxyl number of around of 65 mg KOH/g sample or less, an average number of hydroxyl functionality of 2.5 or less, and viscosity at 25°C of less than approximately 4 Pa s.

[0017] Tanaka et al., Bioresource Technology (2008) 99, 3810-3816 describes the preparation and characterization of polyurethane foams using a palm oil-based polyol. At the first stage, palm oil was converted to monoglycerides as a new type of polyol by glycerolysis. A yield of the product reached 70% at reaction temperature of 90°C by using an alkali catalyst and a solvent.

[0018] Chuayjuljit et al., Journal of Reinforced Plastics and Composites (2008) 29, 218-225 describes the preparation and properties of palm-oil based rigid polyurethane nanocomposite foams.

[0019] Chian et al., Journal of Applied Polymer Science (1998) 68, 509-515 describes a development in polyurethane foam technology, whereby a renewable source of polyol derived from refined-bleached-deodorized palm oil is used to produce polyurethane foams.

[0020] While the prior art has searched for solutions to the technical problem, which is to provide methods for obtaining "green" polyols, that is, from vegetable oils which include palm oil, as well as obtaining polyurethane foams from of these "green" polyols with properties that allow their application in the different uses mentioned above, none of the documents of the prior art refers to a procedure for obtaining polyols derived from palm oil for the preparation of polyurethane, in which two methods of preparation are combined to grant a higher functionality to the final molecular structure. This improves the characteristics of the polyurethane obtained from said polyol, conferring properties such as greater functionality and greater crosslinking.

[0021] Although in other inventions polyols have been obtained from vegetable oils, the products prepared from such polyols are brittle due to the concentration of hydroxyl groups at only one end of the carbon chain.

[0022] Additionally and in relation to the conditions of operation of the glycerolysis method, the present invention achieved decreasing the reaction temperature for obtaining a polyol with favorable results regarding the decrease in energy costs.

[0023] The present invention provides a simple method for its realization, is not expensive, and gives the end result of a product with high technical and functional qualities that places it above those of conventional type and within the same line found in the prior art, with the advantage of having in its raw materials a polyol from renewable natural sources.

[0024] The produced polyols, that are not part of the invention as claimed, have molecular weights between 314 and

3366 and a hydroxyl number between 50 and 450 mg KOH/g sample.

[0025] The resulting rigid foams, that are not part of the invention as claimed, were tested for the density (according to ASTM C373-88) with results between 0.284 and 0.658 g/cm^3, Young's modulus (according to ASTM D695-10) with results between 8.94522 and 54.92330 MPa, and maximum effort (according to ASTM D695-10) with results between 0.92037 and 8.29101 MPa.

[0026] The resulting semi-rigid foams, that are not part of the invention as claimed, were tested for density (according to ASTM C373-88) with results between 0.129 and 0.158 g/cm^3, Young's modulus (according to ASTM D695-10) with results between 0.78727 and 1.54311 MPa, and maximum effort (according to ASTM D695-10) with results between 0.07012 and 0.09753 MPa.

DESCRIPTION OF THE INVENTION

[0027] The present invention is related to the production process of a polyol from palm oil.

[0028] On the one hand, there is provided a method for obtaining monomeric polyols from palm oil that have a hydroxyl number of between 50 and 450 mgKOH/g sample.

[0029] The methods of the present application for the production of polyols are based on the following mother routes:

- Route 1: maleinization of the fatty acids of palm oil
- Route 2: glycerolysis of palm oil does not fall under the invention as claimed
- Route 3: transesterification of palm oil
- Route 4: epoxidation of unsaturated carbon-carbon bonds in palm oil

[0030] Additionally, other modalities of the invention allow obtaining polyol from the combination of these mother routes.

[0031] Specifically, route 1 begins with the alcoholysis of palm oil to obtain fatty acids, which undergo a maleinization process in order to introduce carboxylic groups and from these to extend the glycerin chain and so obtain a polyol from palm oil.

[0032] In the mother route 2, not part of the claimed invention, monoglycerides are prepared from the palm oil but, in contrast to route 1, no maleinization is performed. Rather, polyol is obtained from the palm oil by means of glycerolysis. The glycerolysis takes place at temperatures between 170 and 280°C, obtaining higher reaction speeds the higher the temperature. It is recommended not to exceed 260°C in any case, provide a good system of agitation (350 to 420 rpm) and to use an inert atmosphere (Nitrogen, argon or CO2).

[0033] The process of glycerolysis is usually performed in the presence of a solvent and a catalyst. The selection of a good catalyst allows using lower temperatures.

[0034] The glycerolysis reaction should be carried out under the action of a catalyst that can be homogeneous (acid or base) or heterogeneous. Examples of the catalysts to obtain mono and di glycerides include lead acetate, calcium acetate, lead oxide and lithium ricinoleate, sulfuric acid, hydrochloric acid, sulfonic acid and sodium hydroxide.

[0035] Lead and calcium acetates, as well as the lithium ricinoleate, allow obtaining an excellent glycerolysis in the minimum time (40 to 50 minutes) and at a relatively moderate temperature (235 to 240°C) and, more importantly, using minimum amounts of catalyst.

[0036] The mother route 3 of the present invention corresponds to the preparation of a polyol from palm oil modified through transesterification with pentaerythritol, which is useful when a considerable increase in tensile, hardness and resistance to chemical attack properties is required. This is due to a higher degree of crosslinking caused by the increase in the content of hydroxyl groups.

[0037] In mother route 4 of the present invention a polyol from palm oil is produced by double link epoxidation, in which a process of methanolysis of the palm oil is initially performed to obtain fatty acid methyl esters (FAME), which are submitted to a process of epoxidation with hydrogen peroxide to generate performic acid *in situ.*

[0038] Polyurethanes are prepared from the polyols obtained through any of the four routes or through a combination of the same.

[0039] The polyurethanes are produced through the reaction of a mixture of polyol obtained through the present invention, a commercial polyol, a surfactant, a catalyst and an isocyanate. The polyurethanes may be foams of high density rigid polyurethane.

[0040] The specific characteristics, advantages and novel characteristics of this invention will be established in the following section of the description, corresponding to the detailed description of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0041]

Figure 1 shows a flow chart exemplifying the production of a polyol from palm oil through Route 1.

Figure 2 shows a flow chart exemplifying the production of a polyol from palm oil through Route 2 which does not fall under the invention as claimed.

Figure 3 shows a flow chart exemplifying the production of a polyol from palm oil through Route 3.

Figure 4 shows a flow chart exemplifying the production of a polyol from palm oil through Route 4.

Figure 5 shows a flow chart exemplifying the production of a polyol from palm oil through the combination of Route 4 and Route 2.

DETAILED DESCRIPTION THE INVENTION

[0042] The present invention relates to a process for the production of a polyol from palm oil.

[0043] The processes for the production of the polyols based on palm oil will be described by referring to Figures 1 to 5.

[0044] Figure 1 describes route 1 in a general manner. Secifically, this route includes two different methods, the first comprising the maleinization of palm oil through heating of the same and its mixture with maleic anhydride. The mixture is later reacted in the presence of reflux condenser and an inert atmosphere, and the reaction happens there during an established period, obtaining the polyol.

[0045] The second method, not falling under the invention as claimed, corresponds to the maleinization of fatty acids, beginning with a mixture of palm oil and sodium hydroxide and an ethanol-water solution. The mixture obtained is heated and stirred. Subsequently, a small amount of concentrated sulfuric acid is added, showing the separation of the organic phase and the aqueous phase. Then, saturated sodium chloride solution is added. After the complete separation of the phases, the aqueous phase is eliminated. By means of warming and agitation of the organic phase the fatty acids may be obtained, which are mixed with previously blocked glycerol through an MEK (Methyl ethyl ketone) reaction, carried out with sulfonic toluene acid as a catalyst and toluene as a solvent. The fatty acids then react with the glycerol blocked in the presence of a catalyst, toluenesulfonic acid, and heat. The product of this reaction is evaporated to obtain blocked monoglyceride, which subsequently reacts in a nitrogen and maleic anhydride atmosphere. Sulfuric acid is added to the product of this reaction. The organic phase obtained is washed and submitted to evaporation to finally obtain the polyol.

[0046] Thus, Figure 2 summarizes route 2 which corresponds to the production of polyol from palm oil through glycerolysis. This route comprises the reaction between the palm oil and glycerol, tert-butanol as a solvent and sodium hydroxide as a catalyst in the presence of heat. The product of this reaction is neutralized with hydrochloric acid and submitted to evaporation for elimination of the solvent. The phase obtained is separated through the addition of n-hexane, allowing the residual glycerin to be discarded from the polyol finally obtained.

[0047] Figure 3 summarizes route 3, related to the production of polyol from palm oil modified through transesterification with pentaerythritol. This route comprises the reaction between palm oil, pentaerythritol and lead oxide in the presence of heat with continuous agitation and in an inert nitrogen atmosphere. The product of the reaction is treated with n-hexane, allowing formation of two phases: the precipitate that contains glycerol is then discarded and the other phase is submitted to evaporation to obtain the polyol.

[0048] On the other hand, route 4 is summarized in Figure 4 and comprises a process of epoxidation of the fatty acid methyl esters of (FAME), which are previously obtained through methanolysis of palm oil. This methanolysis comprises the reaction between the palm oil and methanol in presence of sodium hydroxide. Subsequently the glycerin phase is discarded and the phase of interest is washed with phosphoric acid, discarding the solids formed and neutralizing. The product (FAME) is submitted to evaporation to remove the excess methanol.

[0049] In this way, the FAME are made to react with formic acid in the presence of hydrogen peroxide. The reaction is evidenced by the color change from orange to clear yellow. Subsequently, the product is washed with water, sodium bicarbonate and sodium chloride, neutralizing the solution, which then undergoes evaporation to remove the moisture and allows obtaining the polyol.

[0050] Figure 5 describes other modalities of the invention, which correspond to the combination of routes 2 and 4 and are established in more detail below.

[0051] One of these modalities allows obtaining polyol from the olein phase of crude palm oil using lead oxide as a catalyst. The method is then carried out through the epoxidation of the olein phase of crude palm oil with formic acid, in the presence of heat. Subsequently hydrogen peroxide is added and stirred. The reaction is evidenced by the change of color from orange to clear yellow. The product of the reaction is washed with water, sodium bicarbonate and sodium chloride, discarding the aqueous phase and subjecting the organic phase to glycerolysis (reaction with glycerin) using lead oxide as catalyst to thus obtain the polyol.

[0052] Another mode of the invention corresponds to obtaining the polyol from the olein phase of crude palm oil using NaOH as a catalyst. This mode comprises the same steps mentioned for the previous mode, with the difference that the glycerolysis of the organic phase is done in the presence of sodium hydroxide, with a posterior neutralization of the excess catalyst with phosphoric acid.

[0053] Yet another mode of the invention allows obtaining polyol from the olein phase of refined, bleached and deodorized palm oil (RBD). For this purpose the same steps are used as for the previous embodiments, using the raw material mentioned and sodium hydroxide as a catalyst in the glycerolysis.

[0054] The last mode corresponds to obtaining polyol from the olein phase of refined, bleached and deodorized palm oil (RBD), but employing lead oxide as catalyst. In the same way, the steps already mentioned above are used, with the exception that the olein phase of RBD is used as raw material and lead oxide as catalyst in the glycerolysis.

[0055] The routes and modalities described thus allow obtaining the polyurethane foams through the reaction of the polyols produced with methylene diphenyl diisocyanate (MDI).

[0056] For said purpose, the polyol obtained is mixed with a short chain polyol (diethylene 1,6 butanediol), a catalyst (dibutyltin dilaurate, tin octoate, tertiary amine catalysts), water, a surfactant (Silicone or organosiloxane-based), and methylene diphenyl diisocyanate (MDI). The reaction leads to the formation of foam of rigid polyurethane.

[0057] Depending on the hydroxyl number obtained for the polyol, flexible, semi-rigid and rigid polyurethane foams may be obtained, as indicated below:

Hydroxyl No.	50	100	150	200	250	300	350	400
Foam Type	Flexible			Semi-rigid			Rigid	

[0058] Within the applications that these types of foam have, the following may be noted:

Polyurethane	**Application**
Rigid	Molded parts, soles for footwear
Semi-rigid	Thermal insulation, soundproofing insulation, waterproofing, floral foam, chairs adapted to the user (mainly for disabled people)
Flexible	Foam for bras, mattresses

EXAMPLES

[0059] The following examples are presented with the purpose of illustrating the invention and are in no way a limitation, inasmuch as the person moderately skilled in the matter can recognize the possible variations.

EXAMPLE 1 - Obtaining polyol using the first method of route 1

[0060] 300 grams of palm oil were laced in the 250 ml reaction flask. Separately, 65.7 grams of maleic anhydride were weighed and were added to the reaction flask. The same was heated to 180°C. Subsequently the reflux condenser was adapted and the reaction flask placed on a heating iron with magnetic agitation to 1300 allowing the reaction to take place for 3 hours under a nitrogen atmosphere. The product of this reaction is the maleinised oil that was cooled to 100°C and to which an amount of 30.85 g of glycerol was added. The reaction was allowed to continue and the acidity index was tracked every 30 minutes up to a value of 90 mg KOH/g sample, thus obtaining the polyol.

EXAMPLE 2 - Obtaining polyol using the second method of Route 1

[0061] 150 grams of palm oil were placed in a 1000 ml precipitation glass. Subsequently 33.5 g of NaOH and 100 ml of a 1:1 ethanol-water solution were added. The reaction was carried out at a temperature of 80°C for 30 minutes. The solution was stirred slightly in manual form. Then, drops of concentrated sulfuric acid were added. The separation of the organic phase and the aqueous phase was then observed. To complete the solution, 100 ml of saturated sodium chloride solution were added. The solution was left at rest while the phases separated. Subsequently the aqueous phase was discarded and the rest was transferred to a separation funnel, washing with hot water. The pH of discarded wash water was measured to verify it was neutral. Separately, the organic phase was transferred to a lateral release Erlenmeyer, the temperature was increased to 80°C, and the phase was stirred continuously; This procedure was carried out in a vacuum. The fatty acids were obtained as a product.

[0062] 70.83 grams of glycerol were separately weighed and placed in a 500 ml reaction flask. Then 62.90 grams of MEK (methyl ethyl ketone) were added together with 1.8 grams of toluenesulfonic acid and 70 ml of toluene. The reaction was carried out at 90°C for 2 hours. In this way the blocked glycerol was obtained.

[0063] To 40 grams of the fatty acids obtained above, 19.5 grams of blocked glycerol were added in a 500 ml reactor. Subsequently 1.8 grams of sulfonic toluene acid were added and the remaining solution underwent heating at 90°C with magnetic agitation of 1200 rpm, leaving the reaction to develop for three and a half hours. Then the product of the reaction was moved to a separation funnel, also washing with hot water and measuring the pH of outgoing wash water until it was neutral. The product of this washing is consecutively put under rotoevaporation for 3 hours at a temperature of 90°C and in vacuum conditions. By these means the blocked monoglyceride was obtained. Afterwards 25 grams of the blocked monoglyceride are taken and placed in a 500 ml reaction flask. Subsequently 9.2 grams of maleic anhydride are added and the reaction is carried out at 200°C with magnetic agitation for 3 hours under a nitrogen atmosphere. The product is left to cool to 100°C without stopping the agitation. Four drops of concentrated sulphuric acid are immediately added slowly, dissolved in 3 ml of distilled water, and allowed to react for another hour. A hot water wash is then carried out and the result left decanting throughout the night.

[0064] The following day the aqueous phase was discarded and the organic phase was rotoevaporated at 80°C for an hour and a half, thus obtaining the polyol.

EXAMPLE 3 - Obtaining polyol using route 2 *not falling under the scope of the invention as claimed

[0065] In a 500 ml reaction flask, coupled with a reflux condenser, a heating surface and a magnetic agitator, 64.5 grams of palm oil were added, along with 40 grams of glycerol, 20 ml of tert-butanol and 4.5 grams of sodium hydroxide. The conditions of operation were, temperature: 90°C, time: 2 hours and agitation: 1300 rpm.

[0066] Once the time of reaction had elapsed the mixture was cooled to temperature and the catalyst neutralized with an HCl solution at 10%, verifying the pH with a paper indicator. The glycerin and the residual solvent were then removed and the product of interest was rotoevaporated to ensure the complete elimination of solvent in the solution. The rotoevaporation temperature was 90°C and was carried out for 3 hours.

[0067] Finally the phases were separated in a separation funnel, where 60 ml of n-hexane were added with vigorous stirring and constant releasing of pressure. The result was left in repose and the bottom phase discarded, which contained residual glycerin. A polyol was obtained with a hydroxyl number value of 523.23 mg KOH/g sample.

EXAMPLE 4 - Obtaining polyol using route 3

[0068] In a 500 ml reaction flask 40.0 grams of palm oil were weighed, along with 4.32 grams of pentaerythritol and 0.02 grams of lead oxide. Subsequently, the flask was placed on a heating surface where the mixture remained in reaction at a temperature of 200°C, with continuous agitation, an inert atmosphere of nitrogen and water reflux condenser for 2 hours. It was then left to cool and 40 ml of n-hexane were added in a separation funnel, stirring and releasing pressure. The phases were allowed to separate to further discard the precipitate and the glycerol. The other phase was submitted to rotoevaporation at 70°C with constant agitation for 3 hours, thus obtaining the polyol, with a hydroxyl number value of 11.86 mg KOH/g sample.

EXAMPLE 5 - Obtaining polyol using route 4

[0069] Initially the methanolysis of palm oil was carried out, in a 500 ml reaction flask, taking 500 grams of palm oil, together with 160.8 g of methanol and 9 grams of sodium hydroxide. The mixture was carried out at a temperature of 70°C with agitation of 1000 rpm for 1 and a half hours.

[0070] After the reaction time, the product was taken to a separation funnel to discard the glycerin phase that was in the bottom. The phase of interest was then washed with 100 ml of 0.015N phosphoric acid at 60°C, the solids formed were discarded, and repeated the wash was repeated with water at 60°C until the pH was neutralized. The phase of interest was then submitted to rotoevaporation for 3 hours at a temperature of 80°C, for removal of excess methanol. The product obtained corresponds to the fatty acid methyl esters (FAME).

[0071] Separately, in a 1000 ml reaction flask, 190 grams of FAME were added along with 7.71 grams of formic acid. The mixture was heated at 40°C and agitated at 800 rpm. 20.85 grams of hydrogen peroxide were then added drop by drop during 1 hour. After the addition of hydrogen peroxide, the reaction continued for 11 hours with constant temperature and agitation. The evidence of the reaction was seen in the change of color from orange to clear yellow. Hot water washes were immediately conducted until the pH increased to 5. Then a washing with 100 ml of bicarbonate sodium solution at 5% and sodium chloride at 5% was performed. The process ended with hot water washes until completely neutralized.

[0072] The resulting mixture was rotoevaporated for 4 hours at 90°C to remove moisture. The polyol was obtained.

EXAMPLE 6 - Obtaining polyol using routes 2 and 4 (epoxidation and glycerolysis) from the olein phase of crude palm oil and using lead oxide as catalyst

[0073] 200 grams of the olein phase of crude palm oil and 9.97 grams of formic acid were placed in a 500 ml reaction flask, coupled with a reflux condenser, a heating surface to achieve a temperature of 50°C, and magnetic agitation to 800 rpm. The reaction was started and 22.11 grams of hydrogen peroxide were added drop by drop, with constant agitation for 90 minutes. The reaction was allowed to continue for 2 hours. The formation reaction of epoxidized oil was evidenced by a change of color from orange to clear yellow.

[0074] Hot water washes were then conducted until a pH close to 5. A wash was performed with a solution of 5% sodium bicarbonate and with a 5% sodium chloride solution. The aqueous phase was discarded through a separation funnel and the organic phase transferred to a lateral release Erlenmeyer, drying in a vacuum for 3 hours at 80°C. The glycerolysis was then carried out with 100 grams of epoxidized oil, 25.72 grams of glycerin and 0.03 grams of PbO in a 500 ml reaction flask coupled with a reflux condenser, at a temperature of 215°C, and agitation of 1300 rpm for 45 minutes. The polyol obtained was analyzed, resulting in hydroxyl numbers of between 60 and 110 mg KOH/g sample.

EXAMPLE 7 Obtaining polyol using routes 2 and 4 (epoxidation and glycerolysis) from of the olein phase of crude palm oil and using sodium hydroxide as catalyst

[0075] 200 grams of the olein phase of crude palm oil and 9.97 grams of formic acid were placed in a 500 ml reaction flask coupled with a reflux condenser, a heating surface to reach a temperature of 50°C and magnetic agitation to 800 rpm. The reaction was initiated and 22.11 grams of hydrogen peroxide were added drop by drop, with constant agitation during 90 minutes. The reaction continued for 2 additional hours. The reaction of formation of epoxidized oil was evidenced by a change of color from orange to clear yellow.

[0076] Hot water washes were then carried out up to a pH close to 5. A wash was performed with a of 5% sodium bicarbonate solution and with a 5% sodium chloride solution. The aqueous phase was discarded through a separating funnel and the organic phase was transferred to a lateral release Erlenmeyer, drying in a vacuum for 3 hours at 80°C. Subsequently the glycerolysis was performed with 100 grams of epoxidized oil, 25.72 grams of glycerin and 1 gram of NaOH in a 500 ml reaction flask coupled with a reflux condenser, temperature of 180°C and agitation at 1300 rpm for 45 minutes.

[0077] The catalyst was neutralized with drops of phosphoric acid, thus avoiding the formation of soaps. Finally, the polyol obtained was analyzed. It yielded hydroxyl numbers between 400 and 440 mg KOH/g sample.

EXAMPLE 8 - Obtaining polyol using routes 2 and 4 (epoxidation and glycerolysis) from the olein phase of refined bleached deodorized crude palm oil and using sodium hydroxide as catalyst

[0078] 200 grams of the olein phase of crude palm oil and 9.97 grams of formic acid were placed in a 500 ml reaction flask, coupled with a reflux condenser, a heating surface to achieve a temperature of 50°C, and magnetic agitation to 800 rpm. The reaction was initiated and 22.11 grams of hydrogen peroxide were added drop by drop, with constant agitation during 90 minutes. The reaction continued for 2 additional hours. The reaction of formation of epoxidized oil was evidenced by a change of color from orange to clear yellow.

[0079] Hot water washes were then carried out up to a pH close to 5. A wash was performed with a of 5% sodium bicarbonate solution and with a 5% sodium chloride solution. The aqueous phase was discarded through a separating funnel and the organic phase was transferred to a lateral release Erlenmeyer, drying in a vacuum for 3 hours at 80°C. Subsequently the glycerolysis was performed with 100 grams of epoxidized oil, 25.72 grams of glycerin and 1 gram of NaOH in a 500 ml reaction flask coupled with a reflux condenser, temperature of 180°C and agitation at 1300 rpm for 45 minutes.

[0080] The catalyst was neutralized with drops of phosphoric acid, thus avoiding the formation of soaps. Finally, the polyol obtained was analyzed. It yielded hydroxyl numbers between 370 and 420 mg KOH/g sample.

Example 9 - Obtaining polyol using routes 2 and 4 (epoxidation and glycerolysis) from the olein phase of refined bleached deodorized crude palm oil and using lead oxide as catalyst

[0081] 200 grams of the olein phase of crude palm oil and 9.97 grams of formic acid were placed in a 500 ml reaction flask, coupled with a reflux condenser, a heating surface to achieve a temperature of 50°C, and magnetic agitation to

800 rpm. The reaction was initiated and 22,11 grams of hydrogen peroxide were added drop by drop, with constant agitation during 90 minutes. The reaction continued for 2 additional hours. The reaction of formation of epoxidized oil was evidenced by a change of color from orange to clear yellow.

[0082] Hot water washes were then carried out up to a pH close to 5. A wash was performed with a 5% sodium bicarbonate solution and with a 5% sodium chloride solution. The aqueous phase was discarded through a separating funnel and the organic phase was transferred to a lateral release Erlenmeyer, drying in a vacuum for 3 hours at 80°C. Subsequently the glycerolysis was performed with 100 grams of epoxidized oil, 25.72 grams of glycerin and 0.3 grams of PbO in a 500 ml reaction flask coupled with a reflux condenser, temperature of 180°C and agitation at 1300 rpm for 45 minutes.

[0083] Finally, the polyol obtained was analyzed. It yielded hydroxyl numbers between 80 and 90 mg KOH/g sample.

EXAMPLE 10 - Preparation of a polyurethane varnish from polyol obtained by route 1 of the first method *not falling under the scope of the invention as claimed

[0084] The pre-polymer was formed taking 30 g of polyol, 76.92 g surfactant and 20 ml of MEK (Methyl ethyl ketone) in a 250 ml reaction flask at 50°C for 30 minutes. The pre-polymer was then transferred to a precipitate flask of 1000 ml and 14.88 grams of TDI (Toluene diisocyanate) were added, and stirred mechanically for 3 hours maintaining temperature at 70°C. Once the reaction was completed the pre-polymer was cooled to 50°C and 4.96 grams of MEKO (Methyl ethyl ketoxima) were added to block the free NCO groups. This reaction took place for 2 hours. Finally, 2.88 grams of TEA (Triethylamine) were added during 30 minutes with vigorous agitation maintaining the temperature at 50°C. An amount of 50% w/w of water was then added drop by drop to form an emulsion.

EXAMPLE 11 - Preparation of a polyurethane varnish from polyol obtained by route 1 of the second method *not falling under the scope of the invention as claimed

[0085] The pre-polymer was formed taking 12 g of polyol, 50 g surfactant and 10 ml of MEK (methyl ethyl ketone) in a 250 ml reaction flask at 50°C for 30 minutes. The pre-polymer was then transferred to a precipitate flask of 1000 ml and 12.52 grams of TDI (Toluene diisocyanate) were added, and stirred mechanically for 3 hours maintaining temperature at 70°C. Once the reaction was completed the pre-polymer was cooled to 50°C and 5 grams of MEKO (methyl ethyl ketoxima) were added to block the free NCO groups. This reaction took place for 2 hours. Finally, 2.2 grams of TEA (Triethylamine) were added during 30 minutes with vigorous agitation maintaining the temperature at 50°C. An amount of 50% w/w of water was then added drop by drop to form an emulsion.

EXAMPLE 12 - Preparation of a polyurethane foam from polyol obtained by route 2 *not falling under the scope of the invention as claimed

[0086] 9 g of palm polyol were taken and a mixture 50:50 performed with diethylene glycol, placed on a heating surface with magnetic agitation to 800 rpm, and then 0.04 g of surfactant, 0.02 g of DBTL (Dibutilin dilaurate) as catalyst and 0.2 g of water were added. Finally, 3.8 g of TDI (Toluene diisocyanate) were added and rapidly stirred manually. This reaction is highly exothermic.

EXAMPLE 13 - Preparation of a foam of polyurethane from polyol obtained with the route 3 *not falling under the scope of the invention as claimed

[0087] 10 g of palm polyol were taken and a mixture 50:50 performed with diethylene glycol, placed on a heating surface with magnetic agitation to 800 rpm, and then 0.27 g of surfactant, 0.19 g of DBTL (Dibutilin dilaurate) as catalyst and 2.69 g of water were added. Finally, 13.2 g of TDI (Toluene diisocyanate) were added and rapidly stirred manually. This reaction is highly exothermic.

EXAMPLE 14 - Preparation of polyurethane foam from polyol obtained by route 4 *not falling under the scope of the invention as claimed

[0088] 10 g of palm polyol and 10 g of DEG (diethylene glycol) were weighed, then 0, 19 g of DBTL (Dibutyltin dilaurate) catalyst were added, followed by 2.69 g of water and 0.27 g of surfactant. This premix was stirred at room temperature for a few minutes and then 13.24 g of MDI were added. This reaction is highly exothermic.

EXAMPLE 15 - Preparation of a polyurethane foam from polyol obtained from example 6 *not falling under the scope of the invention as claimed

[0089] 9 grams of polyol and 1 gram of 1,6 butanediol were premixed and submitted to heating in case that the polyol was in a solid state. 0.15 grams of silicone 193C and 0.03 grams DBTL (Dibutyltin dilaurate) were then added and mixed for homogeneity; and finally 1.98 grams of TDI (Toluene diisocyanate) were added and stirred vigorously. The reaction this is highly exothermic.

EXAMPLE 16 - Preparation of rigid polyurethane from polyol obtained in example 7 *not falling under the scope of the invention as claimed

[0090] 9 grams of polyol and 1 gram of SDR (Diethylene glycol) are mixed. The mixture, which is solid, is heated. 0.15 grams of silicone 193C and 0.03 grams of DBTL (Dibutyltin dilaurate) were added and mixed to achieve homogeneity, and finally 1.98 grams of polymeric MDI (Methylene diisocyanate) are added and stirred vigorously. The reaction is highly exothermic.

EXAMPLE 17 - Preparation of rigid polyurethane from polyol obtained in example 8 *not falling under the scope of the invention as claimed

[0091] 9 grams of polyol and 1 gram of SDR (Diethylene glycol) are mixed. The mixture, which is solid, is heated. 0.15 grams of silicone 193C and 0.03 grams of DBTL (Dibutyltin dilaurate) were added and mixed to achieve homogeneity, and finally 10.5 grams of polymeric MDI (Methylene diisocyanate) are added and stirred vigorously. The reaction is highly exothermic.

EXAMPLE 18 - Preparation of flexible polyurethane from polyol obtained in example 9 *not falling under the scope of the invention as claimed

[0092] 8.5 grams of polyol and 1.5 grams of butanediol are mixed. The mixture, which is solid, is heated. 0.15 grams of silicone 193C, 0.1 grams of water, and 0.03 grams of DBTL (Dibutyltin dilaurate) were added and mixed to achieve homogeneity, and finally 4.28 grams of polymeric TDI (toluene diisocyanate) are added and stirred vigorously. The reaction is highly exothermic.

[0093] A feature of polyols and of products obtained from these, in view of the previous examples, has yielded the following ranges of properties:

> Polyols with molecular weights between 314 and 3366 and with a hydroxyl number between 50 and 450 mgKOH/g sample.

[0094] The rigid foams resulting were tested regarding density (according to ASTM C373-88) with results between 0.284 and 0.658 g/cm^3, Young's modulus (according to ASTM D695-10) with results between 8.94522 and 54.92330 MPa, and maximum effort (according to ASTM D695-10) with results between 0.92037 and 8.29101 MPa.

[0095] The semi-rigid foams resulting were tested regarding density (according to ASTM C373-88) with results between 0.120 and 0.158 g/cm^3, Young's modulus (according to ASTM D695-10) with results between 0.78727 and 1.54311 MPa, and maximum effort (according to ASTM D695-10) with results between 0.07012 and 0.09753 MPa.

EXAMPLE 19 - Additional experimental runs

[0096] Initially we start from the 4 mother routes (Routes 1-4, considering that Route 1 comprises Methods I and II). From these routes other routes are derived in the order below:

Mother Route	Derived Route
1	1
	5
	9
	13
	17
	21
	25
2	2
	6
	10
	14
	18
	22
	26
3	3
	7
	11
	15
	19
	23
	27
4	4
	8
	12
	12
	16
	20
	24
	28

[0097] In the following table the different experimental runs are summarized, defined by the following parameters:

- Route Number
- Polyol preparation:
  - reagents
  - operating conditions
  - evaluation results
- Preparation of polyurethane:
  - reagents
  - operating conditions
  - product characteristics
  - evaluation results

[0098] The abbreviation "NA" indicates that the indicated procedure was not carried out, as it did not become of interest for the inventors.

Claims

1. A method for the production of polyol from palm oil, **characterized by** comprising the following steps:

   a. mixing palm oil with maleic anhydride in a reactor at a temperature between 170°C and 190°C,
   b. heating and agitating the mixture in step a),
   c. coupling the reactor to a reflux condenser,
   d. carrying out the reaction under permanent agitation for 3 hours.

2. A method for the production of polyol from palm oil, **characterized by** comprising the following steps:

   a. mixing, heating and stirring palm oil with sodium hydroxide and a 1:1 solution of ethanol-water
   b. adding concentrated sulphuric acid to the mixture of step a) until the separation of the phases is noted,
   c. adding a saturated solution of sodium chloride to the mixture of step b),
   d. discarding the aqueous phase obtained in step c), after the complete separation of the phases,
   e. washing the organic phase left from step d) with water at a temperature between 70°C and 80°C,
   f. heating and shaking the organic phase of step e) and submitting it to evaporation in a vacuum to obtain the fatty acids,
   g. mixing the fatty acids obtained in step f) with previously blocked glycerol and a catalyst, heating and shaking,
   h. washing the mixture of step g) with water at a temperature between 70°C and 80°C,
   i. separating and discarding the aqueous phase obtained in the step h),
   j. treating the organic phase remaining from step i) through evaporation in a vacuum to obtain blocked monoglyceride,
   k. adding maleic anhydride to the blocked monoglyceride from step j), heating and shaking in a low nitrogen atmosphere,
   l. cooling the mixture from step k) to 100°C,
   m. adding sulfuric acid to the product of the reaction in step l),
   n. washing with water at a temperature between 70°C and 80°C and decanting the product of the reaction obtained in step m),
   o. separating the aqueous phase obtained in step m),
   p. washing the organic phase obtained in step m),
   q. evaporating the organic phase of step n) to obtain the polyol.

3. A method in accordance with claim 2 wherein the heating temperature in step a) varies between 75°C and 85°C and the time of reaction varies between 28 and 32 minutes.

4. A method in accordance with claims 2 and 3 wherein the step of washing e) is performed up to the point where the pH is neutral.

5. A method in accordance with claims 2 to 4 wherein the organic phase of step f) is heated to a temperature between 75°C and 85°C.

6. A method in accordance with claims 2 to 5, wherein the previously blocked glycerol of step g) is obtained through the following steps:

   a. mixing glycerol, MEK (Methyl ethyl ketone), to toluenesulfonic acid as a catalyst and toluene,
   b. heating the mixture of step a) to a temperature between 85 and 95°C for a time between 110 and 130 minutes to obtain blocked glycerol.

7. A method in accordance with claims 2 to 6, wherein the mixture of step f) is heated to a temperature between 75°C and 85°C, for a time between 2 and 3 hours.

8. A method in accordance with claims 2 to 6, wherein the step of washing h) is performed until the pH is neutral.

9. A method in accordance with claims 2 to 8 wherein the evaporation of step j) is carried out at a temperature between 85°C and 95°C and for a period between 3 and 4 hours.

10. A method in accordance with claims 2 to 8 wherein the reaction temperature of step k) varies between 190°C and

210°C and the time of reaction varies between 170 and 190 minutes.

11. A method in accordance with claims 2 to 10 wherein the cooling of step l) is carried out until the mixture acquires a temperature of 100°C, without stopping the agitation.

12. A method in accordance with claims 6 to 11,wherein in step n) the time of reaction varies between 50 and 70 minutes.

13. A method in accordance with claims 6 to 12,wherein the evaporation of step q) is carried out at a temperature between 75°C and 85°C and for a period between 1 and 2 hours.

14. A method for the production of polyol from palm oil, **characterized by** comprising the following steps:

a. Mixing palm oil, pentaerythritol and lead oxide in the presence of heat, agitation and an inert nitrogen atmosphere,
b. cooling the mixture of step a),
c. treating mixture of step b) with n-hexane, allowing the formation of two phases, stirring and releasing the pressure,
d. discarding the precipitate obtained in step c) which contains glycerol,
e. submitting the organic phase to evaporation for obtaining the polyol.

15. A method in accordance with claim 14, wherein the reaction temperature of step a) varies between 195°C and 205°C, and the time of reaction varies between 110 and 130 minutes.

16. A method in accordance with claims 14 or 15, wherein in step b) the mixture is left to cool to ambient temperature.

17. A method in accordance with claims 14 to 16, wherein the evaporation of step e) is carried out at a temperature between 65°C and 75°C and during a period between 2 and 3 hours.

18. Method for the production of polyol from palm oil, **characterized by** comprising the following steps:

a. producing fatty acid methyl esters (FAME) from the following steps:

- mixing palm oil, methanol and sodium hydroxide at a temperature - between 65°C and 75°C and agitate during a period between 1 and 2 hours,
- discarding the glycerin phase that is at the bottom after the previous reaction,
- washing the phase of interest obtained in the first step with 0,015N phosphoric acid at a temperature between 55°C and 65°C,
- discarding the solids formed,
- washing the product obtained in the previous step with water at a temperature between 55°C and 65°C until the pH this is neutral,
- evaporating the product of the previous step (FAME) to remove excess methanol at a temperature between 75°C and 85°C and during a period between 2 and 3 hours.

b. mixing FAME obtained in step a) with formic acid in the presence of hydrogen peroxide,
c. washing the product obtained in step b) with water at a temperature between 50°C and 60°C,
d. washing the product obtained in step c) with sodium bicarbonate at 5%,
e. washing the product obtained in step d) with sodium chloride at 5%,
f. washing the product obtained in step e) with water at a temperature between 50°C and 60°C,
g. evaporating the solution obtained in step c) to remove the moisture thereby obtaining the polyol.

19. A method in accordance with claim 18, wherein the reaction temperature in step b) varies between 40°C and 50°C and the time of reaction varies between 10 and 11 hours, after of the addition of hydrogen peroxide.

20. A method in accordance with claims 18 or 19, wherein the washing step c) is performed until the pH of the solution is 5.

21. A method in accordance with claims 18 to 20, wherein the washing in step f) is performed until the pH is neutral.

22. A method in accordance with claims 18 to 21, wherein the evaporation of step g) is carried out at a temperature between 70°C and 90°C and for a period between 3 and 4 hours.

23. A method for the production of polyol from palm oil, **characterized by** comprising the following steps:

a. mixing a source of palm oil with formic acid, in the presence of heat,
b. adding hydrogen peroxide to the mixture of step a) and shaking,
c. washing the reaction product of step b) with water, at a temperature between 55°C and 65 °C,
d. washing the product obtained in step c) with sodium bicarbonate at 5%,
e. washing the reaction product of step d) with water, at a temperature between 55°C and 65°C,
f. washing the product obtained in step e) with sodium chloride at 5%,
g. discarding the aqueous phase obtained in step f),
h. drying to the empty the remaining organic phase of step f),
i. mixing the epoxidized oil obtained in step g) with glycerol and catalyst in the presence of heat and agitation.

24. A method in accordance with claim 23, wherein the source of palm oil in step a) is the olein phase of crude palm oils.

25. A method in accordance with claim 23, wherein the source of palm oil in step a) is the olein phase of refined bleached and deodorized palm oil (RBD).

26. A method in accordance with claims 23 to 25, wherein the catalyst of step h) is lead oxide.

27. A method in accordance with claims 23 to 25, wherein the catalyst of step h) is sodium hydroxide.

28. A method in accordance with claims 23 to 25, wherein the washing of step c) is performed until the pH of the solution is 5.

29. A method in accordance with claims 23 to 28, wherein the reaction temperature of step b) varies between 45°C and 55°C and the time of reaction varies between 1 and 2 hours after of the addition of hydrogen peroxide.

30. A method in accordance with claims 23 to 28, wherein the reaction temperature of step i) varies between 170°C and 190°C and the time of reaction varies between 40 and 50 minutes.

Patentansprüche

1. Verfahren zur Herstellung von Polyol aus Palmöl, **dadurch gekennzeichnet, dass** es die folgenden Schritte umfasst:

a. das Mischen von Palmöl mit Maleinsäureanhydrid in einem Reaktor bei einer Temperatur zwischen 170°C und 190°C,
b. das Erwärmen und Durchmischen der Mischung aus Schritt a),
c. das Koppeln des Reaktors mit einem Rückflusskühler,
d. das Durchführen der Reaktion unter ständigem Durchmischen für 3 Stunden.

2. Verfahren zur Herstellung von Polyol aus Palmöl, **dadurch gekennzeichnet, dass** das es die folgenden Schritte umfasst:

a. das Mischen, Erwärmen und Rühren von Palmöl mit Natriumhydroxid und einer 1:1-Lösung von Ethanol-Wasser,
b. das Hinzufügen von konzentrierter Schwefelsäure zu der Mischung aus Schritt a), bis die Trennung von Phasen beobachtet wird,
c. das Hinzufügen einer gesättigten Lösung von Natriumchlorid zu der Mischung aus Schritt b),
d. das Verwerfen der wässrigen Phase, erhalten im Schritt c), nach vollständiger Trennung der Phasen,
e. das Waschen der aus Schritt d) verbliebenen organischen Phase mit Wasser bei einer Temperatur zwischen 70°C und 80°C,
f. das Erwärmen und Schütteln der organischen Phase aus Schritt e) und sie wird im Vakuum einer Evaporation unterzogen, um die Fettsäuren zu erhalten,
g. das Mischen der Fettsäuren, erhalten in Schritt f), mit zuvor blockiertem Glycerin und einem Katalysator, Erwärmen und Schütteln,

h. das Waschen der Mischung aus Schritt g) mit Wasser bei einer Temperatur zwischen 70°C und 80°C,
i. das Abtrennen und Verwerfen der wässrigen Phase, erhalten in Schritt h),
j. das Behandeln der organischen Phase, verblieben aus Schritt i), indem im Vakuum evaporiert wird, um blockiertes Monoglycerid zu erhalten,
k. das Hinzufügen von Maleinsäureanhydrid zu dem blockierten Monoglycerid aus Schritt j), Erwärmen und Schütteln in einer Atmosphäre mit wenig Stickstoff,
l. das Abkühlen der Mischung aus Schritt k) auf 100°C,
m. das Hinzufügen von Schwefelsäure zu dem Produkt aus der Reaktion in Schritt 1),
n. das Waschen mit Wasser bei einer Temperatur zwischen 70°C und 80°C und Abdekantieren des Reaktionsproduktes, erhalten in Schritt m),
o. das Abtrennen der wässrigen Phase, erhalten in Schritt m),
p. das Waschen der organischen Phase, erhalten in Schritt m),
q. Evaporation der organischen Phase aus Schritt n), um das Polyol zu erhalten.

3. Verfahren gemäß Anspruch 2, bei dem die Erwärmungstemperatur in Schritt a) zwischen 75°C und 85°C variiert und die Reaktionszeit zwischen 28 und 32 Minuten variiert.

4. Verfahren gemäß Anspruch 2 und 3, bei dem der Schritt des Waschens e) bis zu dem Punkt durchgeführt wird, an dem der pH neutral ist.

5. Verfahren gemäß den Ansprüchen 2 bis 4, bei dem die organische Phase aus Schritt f) auf eine Temperatur zwischen 75°C und 85°C erwärmt wird.

6. Verfahren gemäß den Ansprüchen 2 bis 5, bei dem das zuvor blockierte Glycerin aus Schritt g) durch die folgenden Schritte erhalten wird:

a. das Mischen von Glycerin, MEK (Methylethylketon) zu Toluolsulfonsäure als Katalysator und Toluol,
b. das Erwärmen der Mischung aus Schritt a) auf eine Temperatur zwischen 85 und 95°C für eine Zeit zwischen 110 und 130 Minuten, um das blockierte Glycerin zu erhalten.

7. Verfahren gemäß den Ansprüchen 2 bis 6, bei dem die Mischung aus Schritt f) auf eine Temperatur zwischen 75°C und 85°C für eine Zeit zwischen 2 und 3 Stunden erwärmt wird.

8. Verfahren gemäß den Ansprüchen 2 bis 6, bei dem der Schritt des Waschens h) durchgeführt wird, bis der pH neutral ist.

9. Verfahren gemäß den Ansprüchen 2 bis 8, bei dem das Evaporieren in Schritt j) bei einer Temperatur zwischen 85°C und 95°C für eine Dauer zwischen 3 und 4 Stunden durchgeführt wird.

10. Verfahren gemäß den Ansprüchen 2 bis 8, bei dem die Reaktionstemperatur in Schritt k) zwischen 190°C und 210°C variiert und die Reaktionszeit zwischen 170 und 190 Minuten variiert.

11. Verfahren gemäß den Ansprüchen 2 bis 10, bei dem das Abkühlen in Schritt 1) durchgeführt wird, bis die Mischung eine Temperatur von 100°C erreicht, ohne dass das Durchmischen gestoppt wird.

12. Verfahren gemäß den Ansprüchen 6 bis 11, bei dem in Schritt n) die Reaktionszeit zwischen 50 und 70 Minuten variiert.

13. Verfahren gemäß den Ansprüchen 6 bis 12, bei dem das Evaporieren in Schritt q) bei einer Temperatur zwischen 75°C und 85°C für eine Dauer zwischen 1 und 2 Stunden durchgeführt wird.

14. Verfahren zur Herstellung von Polyol aus Palmöl, **dadurch gekennzeichnet, dass** es die folgenden Schritte umfasst:

a. das Mischen von Palmöl, Pentaerythritol und Bleioxid in Gegenwart von Wärme, Durchmischen und einer inerten Stickstoffatmosphäre,
b. das Abkühlen der Mischung aus Schritt a),
c. das Behandeln der Mischung aus Schritt b) mit n-Hexan, das Ausbilden von zwei Phasen, Rühren und Ablassen des Drucks,

d. das Verwerfen des Präzipitats, erhalten in Schritt c), das Glycerin enthält,
e. die organische Phase wird einer Evaporation unterzogen, um das Polyol zu erhalten.

15. Verfahren gemäß Anspruch 14, bei dem die Reaktionstemperatur in Schritt a) zwischen 195°C und 205°C variiert und die Reaktionszeit zwischen 110 und 130 Minuten variiert.

16. Verfahren gemäß Anspruch 14 oder 15, bei dem in Schritt b) die Mischung auf Raumtemperatur abkühlen gelassen wird.

17. Verfahren gemäß den Ansprüchen 14 bis 16, bei dem das Evaporieren in Schritt e) bei einer Temperatur zwischen 65°C und 75°C und für eine Dauer von 2 bis 3 Stunden durchgeführt wird.

18. Verfahren zur Herstellung von Polyol aus Palmöl, **dadurch gekennzeichnet, dass** es die folgenden Schritte umfasst:

a. das Herstellen von Fettsäuremethylestern (FAME) durch die folgenden Schritte:

- das Mischen von Palmöl, Methanol und Natriumhydroxid bei einer Temperatur zwischen 65°C und 75°C und Durchmischen für eine Dauer zwischen 1 und 2 Stunden,
- das Verwerfen der Glycerinphase, die am Boden nach der vorherigen Reaktion vorliegt,
- das Waschen der Phase von Interesse, erhalten in dem ersten Schritt, mit 0,015 N Phosphorsäure bei einer Temperatur zwischen 55°C und 65°C,
- das Verwerfen der gebildeten Feststoffe,
- das Waschen des Produkts, erhalten in dem vorangehenden Schritt, mit Wasser bei einer Temperatur zwischen 55°C und 65°C bis der pH neutral ist,
- Evaporieren des Produkts des vorangehenden Schritts (FAME) bei einer Temperatur zwischen 75°C und 85°C für eine Dauer zwischen 2 und 3 Stunden, um überschüssiges Methanol zu entfernen,

b. das Mischen von FAME, erhalten in Schritt a), mit Ameisensäure in Gegenwart von Wasserstoffperoxid,
c. das Waschen des Produkts, erhalten in Schritt b), mit Wasser bei einer Temperatur zwischen 50°C und 60°C,
d. das Waschen des Produkts, erhalten in Schritt c), mit 5-%igem Natriumbicarbonat,
e. das Waschen des Produkts, erhalten in Schritt d), mit 5-%igem Natriumchlorid,
f. das Waschen des Produkts, erhalten in Schritt e), mit Wasser bei einer Temperatur zwischen 50°C und 60°C,
g. das Evaporieren der Lösung, erhalten in Schritt c), um Feuchtigkeit zu entfernen, wodurch das Polyol erhalten wird.

19. Verfahren gemäß Anspruch 18, bei dem nach dem Hinzufügen von Wasserstoffperoxid die Reaktionstemperatur in Schritt b) zwischen 40°C und 50°C variiert und die Reaktionszeit zwischen 10 und 11 Stunden variiert.

20. Verfahren gemäß Anspruch 18 oder 19, bei dem der Waschschritt c) durchgeführt wird, bis der pH der Lösung 5 beträgt.

21. Verfahren gemäß den Ansprüchen 18 bis 20, bei dem das Waschen in Schritt f) durchgeführt wird, bis der pH neutral ist.

22. Verfahren gemäß den Ansprüchen 18 bis 21, bei dem das Evaporieren in Schritt g) bei einer Temperatur zwischen 70°C und 90° C für eine Dauer zwischen 3 und 4 Stunden durchgeführt wird.

23. Verfahren zur Herstellung von Polyol aus Palmöl, **dadurch gekennzeichnet, dass** es die folgenden Schritte umfasst:

a. das Mischen einer Palmölquelle mit Ameisensäure in Gegenwart von Wärme,
b. das Hinzufügen von Wasserstoffperoxid zu der Mischung aus Schritt a) und Schütteln,
c. das Waschen des Reaktionsprodukts aus Schritt b) mit Wasser bei einer Temperatur zwischen 55°C und 65°C,
d. das Waschen des Produkts, erhalten in Schritt c), mit 5-%igem Natriumbicarbonat,
e. das Waschen des Reaktionsprodukts aus Schritt d) mit Wasser bei einer Temperatur zwischen 55°C und 65°C,
f. das Waschen des Produkts, erhalten in Schritt e), mit 5-%igem Natriumchlorid,
g. das Verwerfen der wässrigen Phase, erhalten in Schritt f),
h. das vollständige Trocknen der verbliebenen organischen Phase aus Schritt f),
i. das Mischen des epoxidierten Öls, erhalten in Schritt g), mit Glycerin und Katalysator in Gegenwart von Wärme

und Durchmischen.

24. Verfahren gemäß Anspruch 23, bei dem die Palmölquelle in Schritt a) die Ölphase von rohem Palmöl ist.

25. Verfahren gemäß Anspruch 23, bei dem die Palmölquelle in Schritt a) die Ölphase von raffiniertem, gebleichtem und desodoriertem Palmöl (RBD) ist.

26. Verfahren gemäß den Ansprüchen 23 bis 25, bei dem der Katalysator in Schritt h) Bleioxid ist.

27. Verfahren gemäß den Ansprüchen 23 bis 25, bei dem der Katalysator in Schritt h) Natriumhydroxid ist.

28. Verfahren gemäß den Ansprüchen 23 bis 25, bei dem das Waschen in Schritt c) durchgeführt wird, bis der pH der Lösung 5 beträgt.

29. Verfahren gemäß den Ansprüchen 23 bis 28, bei dem nach dem Hinzufügen von Wasserstoffperoxid die Reaktionstemperatur in Schritt b) zwischen 45°C und 55°C variiert und die Reaktionszeit zwischen 1 und 2 Stunden variiert.

30. Verfahren gemäß den Ansprüchen 23 bis 28, bei dem die Reaktionstemperatur in Schritt i) zwischen 170°C und 190°C variiert und die Reaktionszeit zwischen 40 und 50 Minuten variiert.

Revendications

1. Procédé de production d'un polyol à partir d'huile de palme, **caractérisé en ce qu'**il comprend les étapes suivantes :

a. le mélange d'huile de palme avec de l'anhydride maléique dans un réacteur à une température comprise entre 170° C et 190° C,
b. le chauffage et l'agitation du mélange de l'étape a),
c. le couplage du réacteur avec un réfrigérant à reflux,
d. la réalisation de la réaction sous agitation permanente pendant 3 heures.

2. Procédé de production d'un polyol à partir d'huile de palme, **caractérisé en ce qu'**il comprend les étapes suivantes :

a. le mélange, le chauffage et l'agitation d'huile de palme avec de l'hydroxyde de sodium et une solution 1:1 d'éthanol-eau,
b. l'addition d'acide sulfurique concentré au mélange de l'étape a) jusqu'à ce que la séparation des phases soit notée,
c. l'addition d'une solution saturée de chlorure de sodium au mélange de l'étape b),
d. la mise de côté de la phase aqueuse obtenue dans l'étape c), après la séparation complète des phases,
e. le lavage de la phase organique restant après l'étape d) avec de l'eau à une température comprise entre 70° C et 80° C,
f. le chauffage et l'agitation de la phase organique de l'étape e) et la soumission de celle-ci à une évaporation sous vide pour donner les acides gras,
g. le mélange des acides gras obtenus à l'étape f) avec du glycérol précédemment bloqué et un catalyseur, le chauffage et l'agitation,
h. le lavage du mélange de l'étape g) avec de l'eau à une température comprise entre 70° C et 80° C,
i. la séparation et la mise de côté de la phase aqueuse obtenue à l'étape h),
j. le traitement de la phase organique restant après l'étape i) par évaporation sous vide pour donner un monoglycéride bloqué,
k. l'addition d'anhydride maléique au monoglycéride bloqué de l'étape j), le chauffage et l'agitation dans une atmosphère à faible teneur en azote,
l. le refroidissement du mélange de l'étape k) à 100° C,
m. l'addition d'acide sulfurique au produit de la réaction dans l'étape l),
n. le lavage avec de l'eau à une température comprise entre 70° C et 80° C, et la décantation du produit de la réaction obtenu à l'étape m),
o. la séparation de la phase aqueuse obtenue à l'étape m),
p. le lavage de la phase organique obtenue à l'étape m),
q. l'évaporation de la phase organique de l'étape n) pour donner le polyol.

3. Procédé selon la revendication 2, dans lequel la température de chauffage à l'étape a) varie entre 75° C et 85° C, et le temps de réaction varie entre 28 et 32 minutes.

4. Procédé selon les revendications 2 et 3, dans lequel l'étape de lavage e) est réalisée jusqu'au point où le pH est neutre.

5. Procédé selon les revendications 2 à 4, dans lequel la phase organique de l'étape f) est chauffée à une température comprise entre 75° C et 85° C.

6. Procédé selon les revendications 2 à 5, dans lequel le glycérol précédemment bloqué de l'étape g) est obtenu par les étapes suivantes :

a. le mélange de glycérol, de MEC (méthyléthylcétone), à de l'acide toluènesulfonique en tant que catalyseur et à du toluène,
b. le chauffage du mélange de l'étape a) à une température comprise entre 85 et 95° C pendant un temps compris entre 110 et 130 minutes pour donner un glycérol bloqué.

7. Procédé selon les revendications 2 à 6, dans lequel le mélange de l'étape f) est chauffé à une température comprise entre 75° C et 85° C, pendant un temps compris entre 2 et 3 heures.

8. Procédé selon les revendications 2 à 6, dans lequel l'étape de lavage h) est réalisée jusqu'à ce que le pH soit neutre.

9. Procédé selon les revendications 2 à 8, dans lequel l'évaporation de l'étape j) est réalisée à une température comprise entre 85° C et 95° C, et pendant un temps compris entre 3 et 4 heures.

10. Procédé selon les revendications 2 à 8, dans lequel la température réactionnelle de l'étape k) varie entre 190° C et 210° C, et le temps de réaction varie entre 170 et 190 minutes.

11. Procédé selon les revendications 2 à 10, dans lequel le refroidissement de l'étape l) est réalisé jusqu'à ce que le mélange atteigne une température de 100° C, sans arrêt de l'agitation.

12. Procédé selon les revendications 6 à 11, dans lequel à l'étape n), le temps de réaction varie entre 50 et 70 minutes.

13. Procédé selon les revendications 6 à 12, dans lequel l'évaporation de l'étape q) est réalisée à une température comprise entre 75° C et 85° C pendant un temps compris entre 1 et 2 heures.

14. Procédé de production d'un polyol à partir d'huile de palme, **caractérisé en ce qu'**il comprend les étapes suivantes :

a. le mélange d'huile de palme, de pentaérythritol et d'oxyde de plomb en présence de chaleur, sous agitation et dans une atmosphère d'azote inerte,
b. le refroidissement du mélange de l'étape a),
c. le traitement du mélange de l'étape b) avec du n-hexane, la permission de la formation de deux phases, l'agitation et la libération de la pression,
d. la mise de côté du précipité obtenu à l'étape c) qui contient du glycérol,
e. la soumission de la phase organique à une évaporation pour donner le polyol.

15. Procédé selon la revendication 14, dans lequel la température réactionnelle de l'étape a) varie entre 195° C et 205° C, et le temps de réaction varie entre 110 et 130 minutes.

16. Procédé selon les revendications 14 ou 15, dans lequel dans l'étape b) le mélange est laissé à refroidir à la température ambiante.

17. Procédé selon les revendications 14 à 16, dans lequel l'évaporation de l'étape e) est réalisée à une température comprise entre 65° C et 75° C et pendant un temps compris entre 2 et 3 heures.

18. Procédé de production d'un polyol à partir d'huile de palme, **caractérisé en ce qu'**il comprend les étapes suivantes :

a. la production d'esters méthyliques d'acides gras (FAME) par les étapes suivantes :

- le mélange d'huile de palme, de méthanol et d'hydroxyde de sodium à une température comprise entre 65° C et 75° C, et l'agitation pendant un temps compris entre 1 et 2 heures,
- la mise de côté de la phase dans la glycérine qui est au fond après la réaction précédente,
- le lavage de la phase d'intérêt obtenue à la première étape avec de l'acide phosphorique 0,015N à une température comprise entre 55° C et 65° C,
- la mise de côté des matières solides formées,
- le lavage du produit obtenu à l'étape précédente avec de l'eau à une température comprise entre 55° C et 65° Cjusqu'à ce que le pH de celui-ci soit neutre,
- l'évaporation du produit de l'étape précédente (FAME) pour éliminer le méthanol en excès à une température comprise entre 75° C et 85° C, et pendant un temps compris entre 2 et 3 heures,

b. le mélange du FAME obtenu à l'étape a) avec de l'acide formique en présence de peroxyde d'hydrogène,
c. le lavage du produit obtenu à l'étape b) avec de l'eau à une température comprise entre 50° C et 60° C,
d. le lavage du produit obtenu à l'étape c) avec du bicarbonate de sodium à 5 %,
e. le lavage du produit obtenu à l'étape d) avec du chlorure de sodium à 5 %,
f. le lavage du produit obtenu dans l'étape e) avec de l'eau à une température comprise entre 50° C et 60° C,
g. l'évaporation de la solution obtenue à l'étape c) pour éliminer l'humidité afin d'obtenir le polyol.

19. Procédé selon la revendication 18, dans lequel la température réactionnelle à l'étape b) varie entre 40° C et 50° C et le temps de réaction varie entre 10 et 11 heures, après l'addition du peroxyde d'hydrogène.

20. Procédé selon la revendication 18 ou 19, dans lequel l'étape de lavage c) est réalisée jusqu'à ce que le pH de la solution soit de 5.

21. Procédé selon les revendications 18 à 20, dans lequel le lavage de l'étape f) est réalisé jusqu'à ce que le pH soit neutre.

22. Procédé selon les revendications 18 à 21, dans lequel l'évaporation de l'étape g) est réalisée à une température comprise entre 70° C et 90° C et pendant un temps compris entre 3 et 4 heures.

23. Procédé de production d'un polyol à partir d'huile de palme, **caractérisé en ce qu'**il comprend les étapes suivantes :

a. le mélange d'une source d'huile de palme avec de l'acide formique, en présence de chaleur,
b. l'addition de peroxyde d'hydrogène au mélange de l'étape a) et l'agitation,
c. le lavage du produit réactionnel de l'étape b) avec de l'eau, à une température comprise entre 55° C et 65° C,
d. le lavage du produit obtenu à l'étape c) avec du bicarbonate de sodium à 5 %,
e. le lavage du produit réactionnel de l'étape d) avec de l'eau, à une température comprise entre 55° C et 65° C,
f. le lavage du produit obtenu à l'étape e) avec du chlorure de sodium à 5 %,
g. la mise de côté de la phase aqueuse obtenue à l'étape f),
h. le séchage jusqu'au vide de la phase organique restante de l'étape f),
i. le mélange de l'huile époxydée obtenue à l'étape g) avec du glycérol et un catalyseur en présence de chaleur et sous agitation.

24. Procédé selon la revendication 23, dans lequel la source d'huile de palme à l'étape a) est la phase d'oléine d'huiles de palme brutes.

25. Procédé selon la revendication 23, dans lequel la source d'huile de palme dans l'étape a) est la phase d'oléine d'huile de palme blanchie raffinée et désodorisée (RBD).

26. Procédé selon les revendications 23 à 25, dans lequel le catalyseur de l'étape h) est de l'oxyde de plomb.

27. Procédé selon les revendications 23 à 25, dans lequel le catalyseur de l'étape h) est de l'hydroxyde de sodium.

28. Procédé selon les revendications 23 à 25, dans lequel le lavage de l'étape c) est réalisé jusqu'à ce que le pH de la solution soit de 5.

29. Procédé selon les revendications 23 à 28, dans lequel la température réactionnelle de l'étape b) varie entre 45° C et 55° C, et le temps de réaction varie entre 1 et 2 heures après l'addition du peroxyde d'hydrogène.

30. Procédé selon les revendications 23 à 28, dans lequel la température réactionnelle de l'étape i) varie entre 170° C et 190° C, et le temps de réaction varie entre 40 et 50 minutes.

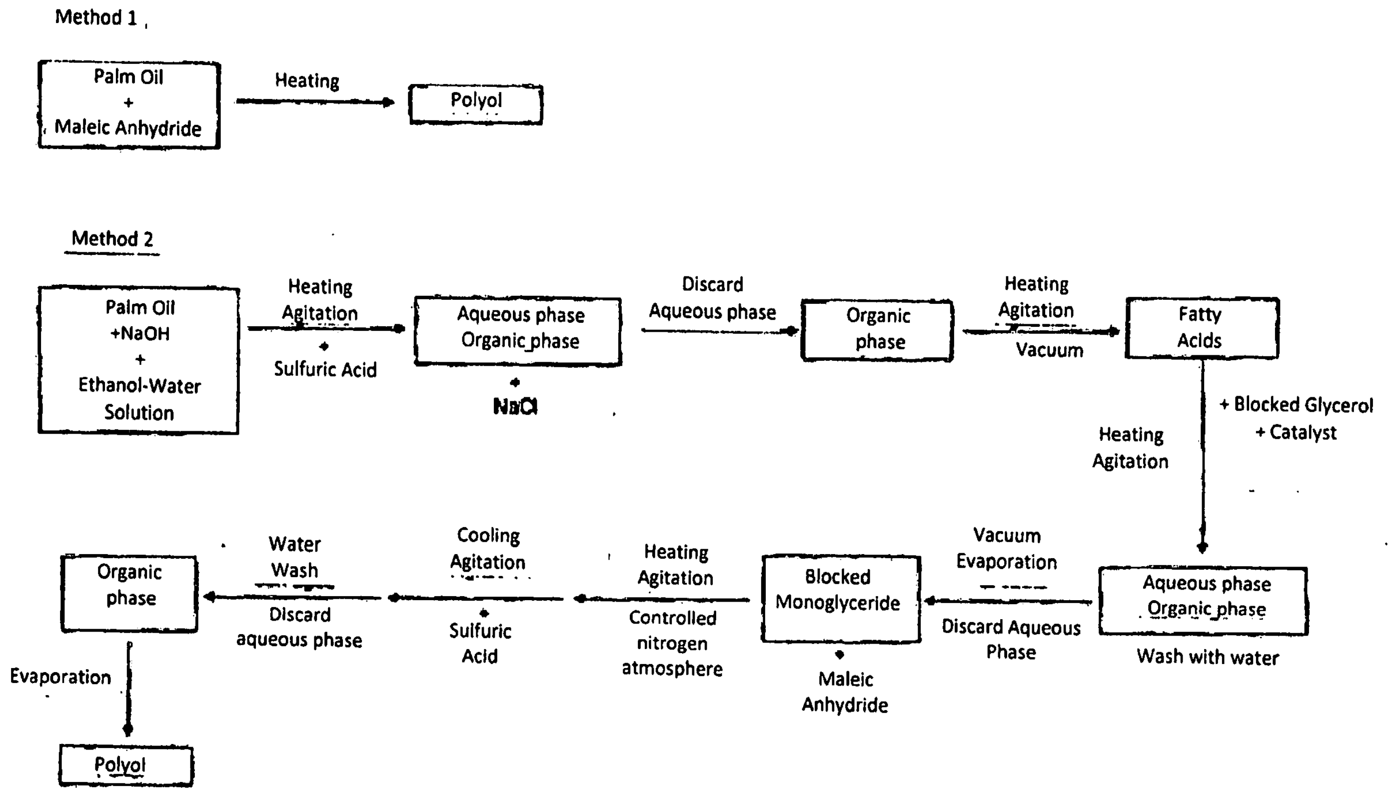

FIG. 1 –Route 1: Maleneisation of palm oil and Maleinisation of fatty acids

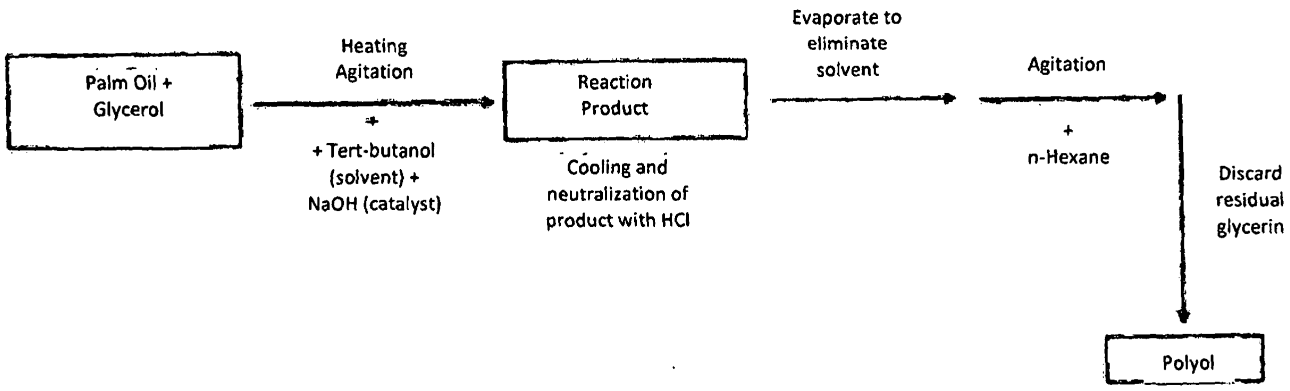

FIG. 2 – Route 2: Glyceroysis of palm oil

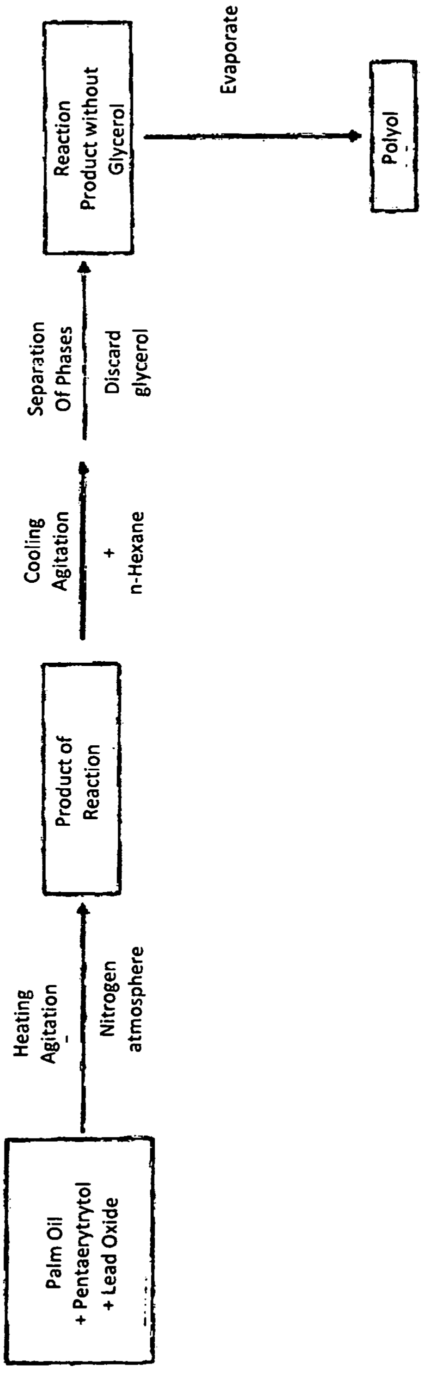

FIG. 3 – Route 3: Transesterification with pentarytrytol

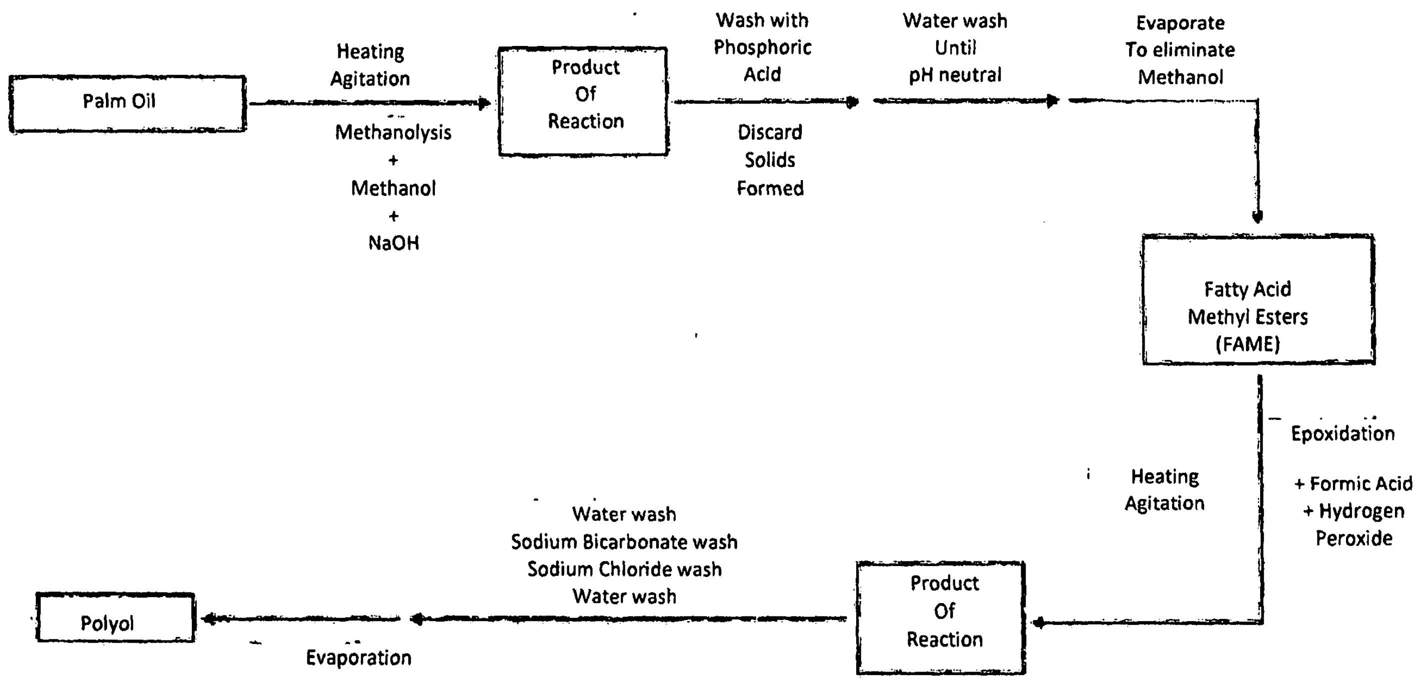

FIG. 4 – Route 4: Epoxidation of the double bond

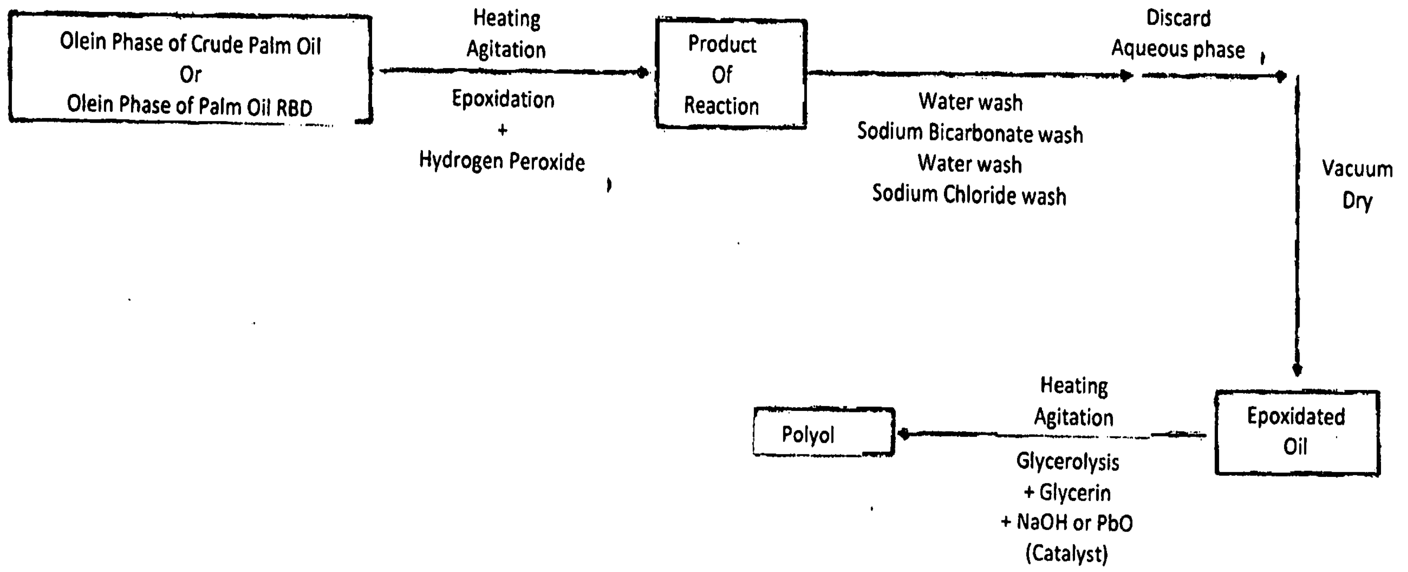

FIG. 5 – Route 4 + Route 2

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