Application of Taguchi design to produce polyols based on castor oil derivatives with diethylene glycol

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Abstract: Castor oil (CO) is one of the most valuable oils, because of its characteristics and potential use in synthesis. A simple way to modify the castor oil structure is the transesterification reaction with an alcohol. Through this reaction, a renewable polyol could be produced and applied in the polyurethane industry. In this study, the transesterification was done by KOH catalysis following a Taguchi experimental design. The chosen alcohol was diethylene glycol (DEG) and the product components were estimated by GPC. This chromatographic technique allowed establishment of the most favorable conditions to produce monosubstituted DEG or disubstituted DEG. In the conditions suggested by the Taguchi design, the condition that favors monosubstituted DEG is 9:1 DEG:CO molar ratios, 200°C for 4 h and 0.5% KOH. This condition leads to approximately 75% monosubstituted DEG and 11% disubstituted DEG in a mixture with the remaining acylglycerols. The hydroxyl value of this product is 407, a high value for a product with a relatively low molecular weight. These characteristics suggest that it can be used as a polyol for polyurethanes.

Keywords: Castor oil; polyol; transesterification; GPC.

Introduction

One of the principal chemical modifications of vegetable oils is the transesterification reaction. There is an extensive discussion about transesterification of oils employing methanol or ethanol to produce biodiesel, a renewable fuel to replace petrodiesel [1]. Not for fuels applications, vegetable oils are a good alternative option as starting materials to produce polyols [2]. The polyurethane industry uses large amounts of petrochemical polyols. To reduce the demand for petrochemicals, more environmentally friendly materials are being developed [3]. Desirable characteristics of these new products include high hydroxyl content, thermal stability, and low viscosity [4]. The crude oil has low reactivity because of its low hydroxyl content. Reactions are needed to introduce more hydroxyl groups and primary hydroxyl groups, such as the transesterification[5]. The polyol monomer used to produce polyester or polyurethane polymer is important for the mechanical properties of the resulting polymer. The selection of polyol can impart a significant effect in inducing hard or soft regions in polyurethanes[6]. Castor oil has been used industrially because of its chemical properties, and has found applications in the synthesis of a series of polyurethanes, such as polyurethane elastomers, adhesives, and coatings [7].

The main fatty acid constituent of castor oil is ricinoleic acid, which has a hydroxyl group at carbon-12 [8]. This fatty acid promotes hydrophobic interactions by the main carbon chain and hydrophilic liks by the esters groups [9]. Polyols from vegetable oils are considered excellent resources employed in industry because they are produced worldwide and are easy to process and low-cost [10]. Modification of castor oil by the transesterification reaction is a simple, low-cost procedure and the structures of the compounds produced are controlled by the reaction conditions used. Xu, using methyl ricinoleate and diethylene glycol at 190-200°C, prepared polyricinoleate diol and used it to prepare polyurethanes with control of the mechanical properties[11]. Many polyhydroxylated compounds are used in transesterification reactions with castor oil. Valero and Gonzalez reported the use of pentaerythritol as a reactant in the transesterification process with castor oil [12]. In this reaction, the catalyst used was PbO at a temperature of 200°C for 2.5 hours of reaction. Valero used PbO and pentaerythritol to prepare diols, and synthesized a network polymer [13]. To increase the thermal stability of polyurethanes, Cakić was reacted castor oil with the product of the glycolysis of PET, introducing aromayic unities to the polyol [14].

The design of experiment is a mathematical tool which function is to provide consistent and feasible analysis of results and predict scenarios and/or interactions. The Taguchi design of experiment is based on a selection of a quality in one matrix and optimizes the conditions factors to accomplish the quality [15]. The design itself is composed by a table where the factors are arranged by an orthogonal array. The number of runs is related to the number of factors, a typical four factors experiment with three levels can be optimized with nine runs [16]. This leads to an economy of time and materials involved in each factor with the benefits of revealing useful information with a reduced number of experiments [17]. To optimize the transesterification of castor oil with methanol, Ramezani studied the effect of reaction temperature, mixing intensity, alcohol to oil ratio and catalyst concentration as factors [16].

The aim of this study was to obtain a new polyol derived from castor oil and diethylene glycol. The study included an attempt to control the reaction products by the use of Taguchi experimental design, and determine the composition of the reaction products by Gel Permeation Chromatography (GPC)/Nuclear Magnetic Ressonance (NMR).

Experimental Section

The castor oil (CO) employed in the transesterification reactions was purchased from Farmanilquima (Curitiba, Brazil). Diethylene glycol (99%), potassium hydroxide (99.5%), and disodium sulfate from Vetec (Rio de Janeiro, Brazil) were used as the reagent, catalyst, and drying agent, respectively. Dichloromethane (99%) from Synth (Diadema, Brazil) was used as the extraction solvent, and tetrahydrofuran (HPLC grade, Vetec) was used as the mobile phase for GPC analysis.

Transesterification of castor oil

In a transesterification reaction, some parameters can influence the formation of the products. In this study, the diethylene glycol (DEG):CO molar ratio, temperature, reaction time and catalyst concentration were evaluated as variables (factors). The statistical model adopted to evaluate those parameters together in three levels was the robust Taguchi design. Table 1 provides details of the nine runs needed to perform the Taguchi design, with the exact values for each variable in each run.

All reaction runs were conducted in a 125 mL round-bottom flask equipped with a magnetic stirrer. Heating was maintained via an oil bath at the specified temperature. In the first step, the amount of castor oil, 50 g (0.05 mol), was weighed. In the second step, the catalyst (KOH) was dissolved in the DEG for alkoxy formation, provided by heating. Then, this solution was added to the weighed castor oil in a round-bottom flask and the reaction started. After the reaction, the flask was cooled to room temperature and the contents transferred to a separatory funnel. A first wash was done with water to remove glycerol and unreacted DEG, followed by solubilization of the ester products in dichloromethane. The product was again washed with water. The ester products were obtained by rota-evaporation of the solvent and retained for analysis. Each run from the Taguchi design was analyzed by GPC, with no other purification procedure, to investigate the profile of the main components.

Table 1. Taguchi design for castor oil transesterification

Run	molar ratio (DEG:CO)	Temperature (°C)	Reaction Time (h)	Catalyst KOH (w:w %)*
1	3:1	150	2	0.1
2	3:1	175	4	0.3
3	3:1	200	6	0.5
4	6:1	150	4	0.5
5	6:1	175	6	0.1
6	6:1	200	2	0.3
7	9:1	150	6	0.3
8	9:1	175	2	0.5
9	9:1	200	4	0.1

*Based on castor oil

In general, the GPC showed the contents of monosubstituted and disubstituted ester of DEG, 2-(2-hydroxyethoxy)ethyl (9Z,12R)-12-hydroxyoctadec-9-enoate and oxybis(ethane-2,1-diyl) (9Z,12R,9'Z,12'R)bis(12-hydroxyoctadec-9-enoate), that could be obtained in the reaction, and unreacted triacylglycerol. After analyzing the results from the GPC combined with the Taguchi design, two new runs were performed in the optimum conditions suggested by the design, focusing on monosubstituted DEG and disubstituted DEG. The optimum conditions to produce monosubstituted DEG (MS-DEG) were: DEG:CO molar ratio 9:1, 200°C for 4 h with 0.5% catalyst; and to produce disubstituted DEG (DS-DEG) were: DEG:CO molar ratio 3:1, 175°C for 18 h with 0.3% catalyst.

An internal standard was made by the hydrolysis of the castor oil, 50g of castor oil, 15g of KOH dissolved in 50g of water and heated at 80°C/2h. The fatty acids salts were neutralized until pH 5 with

concentrated HCl, and the top layer dried in rotary-evaporator. The mixture of free fatty acids was esterified with DEG employing 2%w:w manganese acetate as the catalyst at 175°C for 2 h. The product was washed with water and dried in rotary-evaporator.

Analytical procedures

The ester conversion was monitored by GPC with a methodology similar to Schoenfelder, in a Waters 1515 chromatograph, with a Waters 2487 refractive index detector and two columns in series: Supelco TSK 1000 (<1,500Da) and Waters Styragel 100 (<1500Da). THF was used as the mobile phase at

The products were characterized by FTIR spectra recorded in a Varian 660-IR spectrometer, with 64 scans at 4 cm^{-1} resolution from 400 to 4000 cm^{-1} and KBr discs as the support for film formation. The hydroxyl values were determined following ASTM D 1957-86, with the scale modified, using half quantities. For the optimum conditions, ^{1}H NMR spectroscopy was done in a Bruker DPX200 operating at 4.7 T and 200 MHz. Samples were prepared in deuterated chloroform containing 0.1% TMS.

0.8 mL/min and 40°C column temperature [18]. The relative concentrations of the ester products were determined by normalized areas of peaks. To identify the monosubstituted ester, disubstituted ester, and triacylglycerol, standards of monolein, diolein, and triolein were employed. The peak for the monosubstituted ester comprises the monosubstituted DEG plus monoacylglycerol, and the peak for the disubstituted ester comprises the disubstituted DEG plus diacylglycerol. To distinguish the co-eluted products, NMR spectroscopy was used for the products obtained under the optimized conditions.

Results and Discussion

Figure 1 shows a general scheme for product formation when castor oil reacts with DEG. In the first step, the catalyst (KOH) dissolves in DEG, leading to an alkoxide salt after heating, as proposed by Gok [19]. The reaction of the DEG with the metal hydroxide produces water, which can be eliminated by evaporating since the DEG boiling point is 245°C. This alkoxide salt can react again with another catalyst molecule and generate a di-alkoxide salt. These alkoxides salts react with the triacylglycerol (TAG) once or twice, forming the monosubstituted or disubstituted DEG.
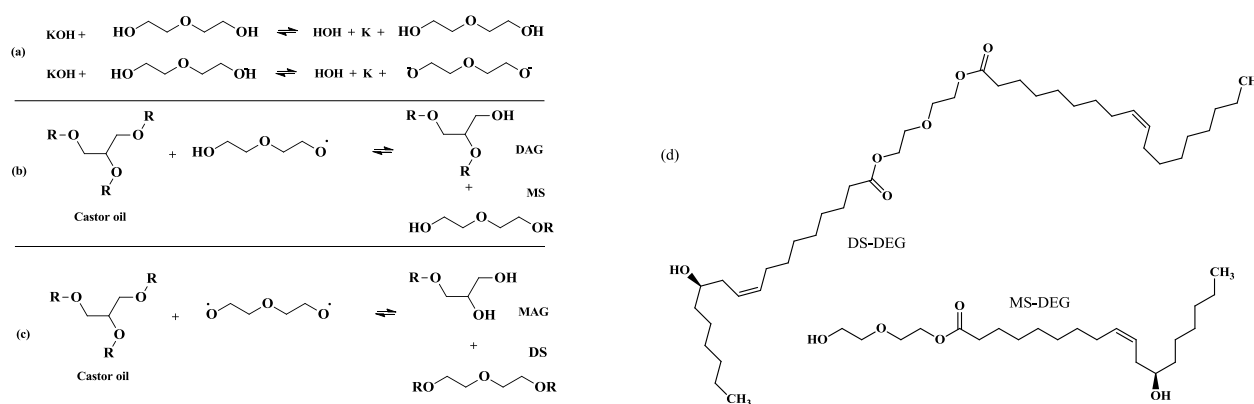
Figure 1. Scheme of alkoxy generation [a], monosubstituted DEG (MS) [b] and disubstituted DEG (DS) [c] formation with the exact structures [d]. R= ricinoleic acid structure, DAG= diacylglycerol and MAG= monoacylglycerol.

The Taguchi design is a helpful tool to evaluate 4 parameters with few runs, affording economies of time and reagents. The mass yield (mass of the material obtained after the rota-evaporation step in % relative to initial CO mass) and reaction conversion (% of products, DS and MS related to initial 100% TAG) are described in Table 2. In general, the transesterification reaction showed a good mass recovery of ester (mass yield), except runs 4 and 7,

in which mass recovery was compromised by emulsification during the water wash step. The values of mass yield above 100% are explained by the molar quantities of the compounds in the transesterification of castor oil with DEG. One mol of castor oil has approximately 933.4g and considering 100% reaction conversion to mono ester of DEG, three mols of MS product generate 1159.8g; which results in 124% of mass yield.

Table 2. Mass yield and composition of esters produced in transesterification with DEG

run	DEG:CO ratio	T (°C)	Time (h)	KOH (w:w%)	Mass Yield (%)	Composition (%)			Reaction conversion (%)
						TAG	DS	MS	DS+MS
1	3:1	150	2	0.1	99.23	82.03	13.47	4.50	17.97
2	3:1	175	4	0.3	101.08	7.57	32.32	60.12	92.44
3	3:1	200	6	0.5	107.46	3.42	36.79	59.79	96.58
4	6:1	150	4	0.5	42.06	4.55	20.12	75.33	95.45
5	6:1	175	6	0.1	113.87	17.11	26.93	55.96	82.89
6	6:1	200	2	0.3	113.55	0.72	19.11	80.16	99.27
7	9:1	150	6	0.3	63.42	9.28	20.01	70.71	90.72
8	9:1	175	2	0.5	104.18	0.83	12.23	86.94	99.17
9	9:1	200	4	0.1	117.41	2.28	15.54	82.19	97.73

Direct evidence of the reaction conversion is the remaining TAG content in each condition. Runs 1 and 7, using the lowest temperature combined with low and medium catalyst concentrations, yielded products with a high TAG content. On the other hand, in run 6, with high temperature and medium catalyst concentration, only 0.72% TAG remained, indicating a high conversion. Cavalcante obtained 97.89% conversion by employing a response surface reacting castor oil and ethanol catalyzed by KOH[20]. The optimized condition in ethanolysis was 11:1 ethanol:castor oil ratio, 90 min and 1.75% KOH. With a similar objective of producing a new polyol, Valero reacted castor oil with pentaerythritol at 210°C for 2 h with 0.05% litharge catalyst and 10% mass of pentaerythritol. The conversion obtained was 21.2% monosubstituted pentaerythritol, 8.5% disubstituted pentaerythritol, with 20.8% DAG, 40.5% MAG and 9% other components remaining[13]. Amiza obtained approximately 40% MAG and 50% DAG from the transesterification of palm oil employing 0.5 KOH as catalyst [14] In this study, except for run 1, the conditions led to a good

conversion reaction, higher than 90%, considering the sum of MS- and DS-DEG determined by GPC. Also, run 8, with a high molar ratio and 175°C, gave approximately 87% yield only in MS-DEG. Clearly, modulating the independent factors changes the quantity of MS- or DS-DEG obtained.

Considering the amount of MS-DEG as a dependent variable, Figure 2 (a) shows the relationship of the Taguchi analysis. This analysis suggests that a high DEG:CO ratio, temperature, and catalyst concentration, and a medium time favored the production of MS-DEG. The principal factor that influenced the MS-DEG was the initial amount of DEG employed; for this set of experiments, the correlation matrix between the quantities of MS-DEG and DEG was 0.68. On the other hand, the Taguchi analysis with DS-DEG as the dependent variable (Figure 2, b) suggested that a low DEG:CO ratio, medium temperature and catalyst concentration, and a long time produced a larger quantity of DS-DEG. In this case the factor with the most impact on DS-DEG was time, with a correlation matrix of 0.69.
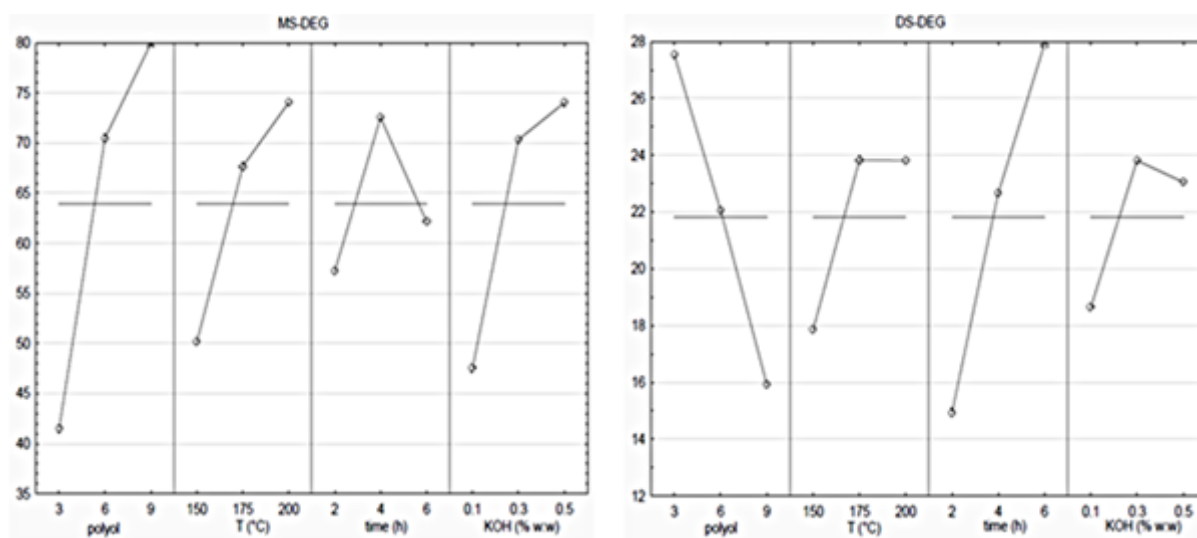
Figure 2. Factor analysis from the Taguchi design.

The FTIR spectroscopy showed a characteristic profile of aliphatic compounds for both the castor oil and transesterification products. This is evident in Figure 3, attributing to castor oil the bands of C-H stretch from the CH_2/CH_3 groups at 2926 and 2956 cm^{-1}, the methyl bend at 1458 and 1377 cm^{-1} (asymmetric and symmetric), and the methylene bend at 1463 cm^{-1}. The ethylene C=C group found in the ricinoleic acid structure (C9-C10) was characterized by C-H stretching and bending at 3007 and 1417 cm^{-1}. Also, the hydroxyl group present on C12 is demonstrated by O-H stretching at 3419 cm^{-1} (associated) and bending at 1352 cm^{-1}, and the C-O stretch from secondary alcohol at 1097 cm^{-1}. The ester group is present at 1745 cm^{-} corresponding to C=O stretch and O-C stretch at 1240 and 1164 cm^{-1}. The spectra obtained from the different runs were similar to each other and also to the castor oil. The bands mentioned above for the experimental runs had very close values to castor oil. The main importance of the FTIR analysis is to emphasize the additional broadening and intensification at O-H stretch 3397 cm^{-1}, presence of primary hydroxyl groups at 1058 cm^{-1} from C-O stretch, and 1126 cm^{-1} corresponding to the ether linkage from DEG [21].
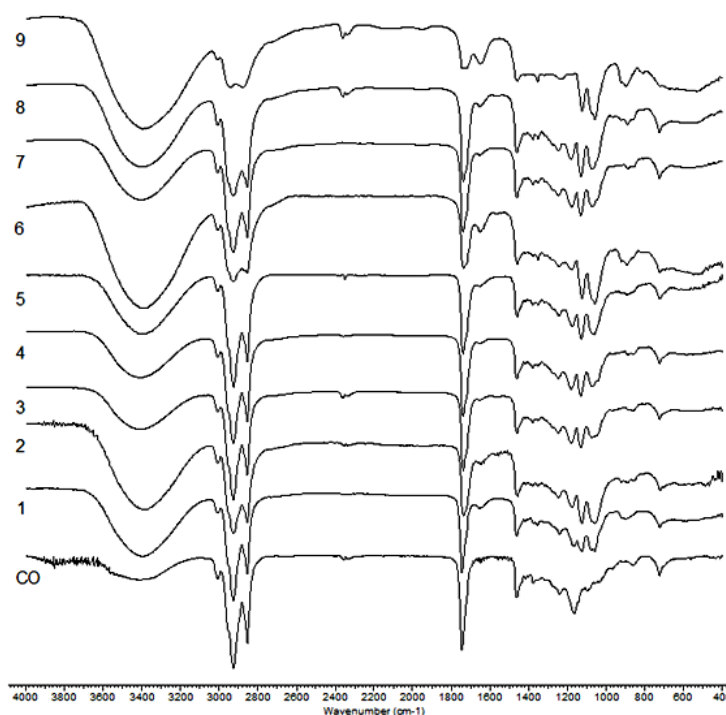
Figure 3. FTIR spectra of the castor oil (CO) and runs under different conditions.

The hydroxyl value determined for the castor oil is similar to those reported by other authors, such as Teramoto in which cator oil showed 161mg KOH/g oil[22]. The oil employed had a hydroxyl value of 159, and the transesterification procedure led to products with higher hydroxyl contents (Table 3). The highest content was obtained with run 9 (OH 492) and run 6 (OH 408); the lowest OH number was obtained in run 4 (227), which is much higher than the castor oil OH value. These high hydroxyl values are important for the production of polyol monomers. In the present study, the products had a relatively low molecular weight. This can influence the hydroxyl content; Xu synthesized a polyol with a moderate molecular weight and a hydroxyl content of 43.5[11]. The starting material of Xu was methyl ricinoleate, with a hydroxyl content of 180. The reaction with DEG was done in two stages: 200°C for 105 min, followed by vacuum at the same temperature for 90 min. The key to obtain the product was the molar ratio employed, 7.7:1 methyl ricinoleate:DEG. Some of the runs shown had a similar hydroxyl content to the product obtained by Valero, 310 (OH number) with 29% of the esters derived from pentaerythritol [13].

Table 3. Hydroxyl content of the transesterification products from castor oil and DEG

Run	Hydroxyl	StdDev	RSD
Castor	159.10	2.27	1.43
1	331.62	19.83	5.98
2	308.35	6.08	1.97
3	263.31	1.22	0.46
4	227.04	0.67	0.29
5	291.39	3.77	1.29
6	408.02	6.86	1.68
7	321.34	9.43	2.93
8	350.60	12.69	3.62
9	492.91	14.31	2.90

*Relative standard deviation

Based on the Taguchi analysis (Figure 2), two new runs were proposed, one focusing on the production of MS-DEG and the other on DS-DEG. The conditions suggested for a maximum MS-DEG yield were a 9:1 DEG:CO ratio, 200°C for 4 h, employing 0.5% catalyst. The suggested conditions to produce DS-DEG were a 3:1 DEG:CO ratio, 175°C for 18 h, with 0.3% catalyst.   The main characteristics of the products are described in Table 4.

Table 4. Compositions of products from conditions suggested by the Taguchi design

run	DEG:CO	T (°C)	Time (h)	KOH	Mass Yield (%)	Composition (%)			
						oligomers	TAG	DS	MS
MS-DEG	9:1	200	4	0.5	122.1	-	0.26	14.67	85.07
DS-DEG	3:1	175	18	0.3	130.7	5.47	5.47	32.9	58.44

In general, the results obtained using the suggested conditions were close to those obtained in the experiments done with the Taguchi experimental design. This indicates that the levels for each factor in the Taguchi design must be chosen with care, so that the Taguchi design is not developed with levels that depart too much from the best value. Both conditions showed contents of MS-DEG and
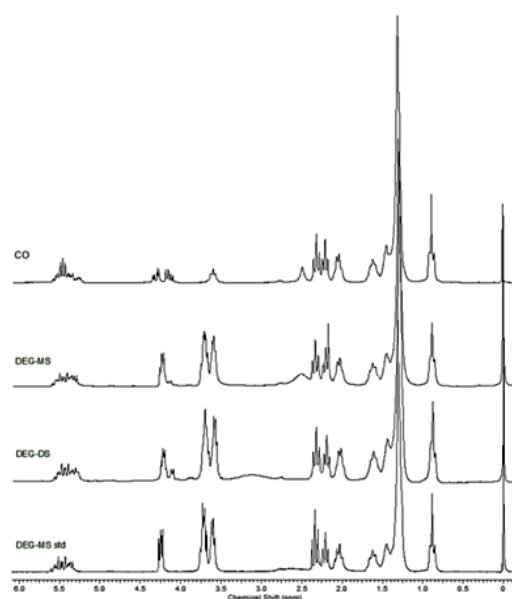
DS-DEG that were similar to some conditions obtained in the experimental design. The difference in the suggested conditions is the remaining quantity of TAG in MS-DEG, which is quite low. The hydroxyl content of MS-DEG was 407.70 ±12.57 (RSD 3.08%) and for DS-DEG was 425.63 ± 18.08 (RSD 4.25%). Again, these values are interesting and important when choosing a candidate polyol monomer.

The approximately 5% TAG remaining in DS-DEG is intriguing. With a longer reaction time, 5% TAG may represent a reversion in the reaction or the beginning of oligomerization, since ricinoleic acid had a hydroxyl group at C12

Figure 4. NMR spectra of suggested conditions from Taguchi design.

There could be an error inherent in the GPC quantification method used.

In this technique the compounds are separated by their molecular weight, and compounds with similar molecular weights may overlap. Another technique was employed to estimate the quantity of acylglycerols and DEG esters. Figure 4 shows the NMR spectra of the products from the suggested conditions.

To determine the best signal to estimate the DEG ester products, a standard compound was synthesized. The free fatty acids from castor oil were esterified with DEG employing manganese acetate as the catalyst at 175°C for 2 h. The goal of this reaction was to synthesize MS-DEG; and its quantity determined by HPLC was above 98%. In the NMR spectrum generated by the synthesized standard, it is clear that the CH_2 group attached to an oxygen from the ester linkage shows a distinct triplet near 4.25 ppm. The other CH_2 groups from the DEG structure generate a group of poorly resolved signals in the range of 3.5-3.75 ppm, restricting their use in quantitative analysis. Compton showed that the 1H NMR spectrum is a useful tool to quantify MAG and DAG[23]. The remaining acylglycerols in the DEG ester products, such as MAG and DAG, showed signals near 3.9, 4.05 and 4.09 ppm, while TAG showed a signal near 5.23 ppm. It is expected that MAG exists as glycerol substituted at C1 or C2. The C1 substituted glycerol is responsible for the signal at 3.9 ppm, and the C2 substituted glycerol signal produces the signal at 4.09 ppm [15].

Table 5. Estimated ester composition (%)

	DEGE	TAG	DAG	MAG*
MS-DEG	84.14	1.99	3.15	10.72
DS-DEG	64.61	1.7	2.52	31.17

*sum of MAG C1 and C2

The use of the NMR technique to estimate components in the ester mixture has advantages and disadvantages. The advantages include the ability to detect each possible compound present in the mixture, rapidity, and economy in use of reagents. In the NMR spectra, the signals from each compound

group appear in a different region. The GPC analysis employed cannot adequately separate MS-DEG from MAG, or DS-DEG from DAG. By NMR, there is a significant quantity of MAG in MS-DEG (Table 5), which was not revealed by the chromatogram. Also, the real conversion for sample MS-DEG was 82.37%, counting both MS- and DS-DEG compounds. One of the disadvantages of NMR in this case is the overlap of the MS- and DS-DEG signals that could be used to quantify components in the mixture. The signal employed is the CH2 group from DEG attached to the O atom of the ester group. This CH2 group has the same neighbor in the MS- and DS-DEG structures, preventing them from being distinguished.

Conclusion

The transesterification of castor oil can be accomplished by employing KOH as a catalyst. This can reduce the cost and toxicity of the process, e.g., compared to lead catalysts. The Taguchi design for the transesterification of castor oil with DEG demonstrates the importance of temperature in this process. To obtain good conversion, higher than 80%, high temperatures are needed. The desired properties of the products, such as more monosubstituted DEG or more disubstituted DEG is linked to the conditions of the reaction. The condition that favors monosubstituted DEG is 9:1 DEG:CO molar ratios, 200°C for 4 h and 0.5% KOH.

The results demonstrated that the GPC can be a helpful technique to monitor and estimate the transesterification products and reaction conversion. Although the MAG is not precisely determined by GPC, this technique is important to monitor the reaction conversion, the change of the oil in to products. The characteristics of each polyol are important for selecting a specific product to use as a new polyol for the polyurethane industry.

Acknowledgments

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