

KINETICS OF THE ESTERIFICATION OF MALEIC ANHYDRIDE WITH CASTOR OIL.

P.C. MAZO[†], D. ESTENOZ[‡], L.A. RÍOS[†]

[†] Grupo Procesos Fisicoquímicos Aplicados. Departamento de Ingeniería Química, Universidad de Antioquia. Calle 67 N° 53-108 Medellín, Tel 2195539

pcmazo@matematicas.udea.edu.co

[‡] Instituto de Desarrollo Tecnológico para la Industria Química (Intec). Santa Fe Argentina

destenoz@ceride.gov.ar

Abstract— Kinetics reaction between castor oil and maleic anhydride without condensation and catalyst was studied. On the other hand, the products concentration, kinetics and thermodynamics parameters were determined using mathematical modeling and were validated with experimental data. The reaction was carried out in a semi-batch reactor at constant temperature. The reaction was conducted through the determining of the acid number (ASTM D4662-03), and showed first order kinetics with respect to the anhydride. For the modified oil, the hydroxyl value (OHv) was quantified through titration following (ASTM D4274-05). The distribution of molecular weights was determined using gel permeation chromatography (GPC), and functional group analysis was determined using infrared spectroscopy (IR).

Keywords— Castor oil, anhydride maleic, esterification, kinetics, mathematical model

I. INTRODUCTION

Castor oil is a viscous pale yellow non-volatile and non-drying oil with a bland taste and is sometimes used as a purgative. India is the world largest exporter of castor oil; other major producers are China and Brazil. The chemistry of castor oil is centered on its high content of ricinoleic acid and the three points of functionality existing in the molecule. These are: (1) the carboxyl group which can provide a wide range of transesterifications, hydrolysis, saponification, reduction; (2) the single point of unsaturation which can be altered by hydrogenation or epoxidation or vulcanization or addition reactions; and (3) the hydroxyl group which can be esterified or acetylated or alkoxylated, may be removed by dehydration to increase the unsaturation of the compound to give a semi-drying oil, can be split at that point by high-temperature pyrolysis and by caustic fusion to yield useful products of shorter chain length. The ricinoleic acid comprises over 89% of the fatty acid of the oil (Ogunniyi, 2006).

Although castor oil is not edible, it is more versatile than other vegetable oils as it is widely used as a starting material for many industrial chemical products because of its unique structure. It is one of those vegetable oils that have found usage in many chemical industries.

It is a raw material for paints, coatings, inks, lubricants and a wide variety of other products.

Because of its hydroxyl functionality, the oil is suit-

able for use in isocyanate reactions to make polyurethane elastomers (Quipeng *et al.*, 1990), polyurethane millable (Yeganeh and Mehdizadeh, 2004), adhesives and coatings (Trevino and Trumbo, 2002; Somani *et al.*, 2003), interpenetrating polymer network from castor oil-based polyurethane (Xie and Guo, 2002) and some semi-rigid polyurethane foams that have potential uses in thermal insulation were produced when castor oil/polyether mixture was reacted with toluene diisocyanate (Ogunniyi *et al.*, 1996).

Maleinization reaction has been used to make chemical modification of vegetable oils through Diels-Alder (conjugated dienes), esterification (alcohols) and “ene” reactions (compounds with allylic hydrogens) with maleic anhydride.

Main modifications that have been made to olefinic compounds with the aim to increase its hydrophilicity are “ene” reactions and many adducts can be prepared through Diels-Alder reactions of unsaturated fatty acids with maleic anhydride. Those products and their derivatives are employed as dry oils, water-soluble paints and surfactants to metals, some applications of these reactions with vegetable oils are described by Bickford *et al.* (1942), Candy *et al.* (2005), Plimmer (1949); Teeter *et al.* (1948), Tomodaa *et al.* (1998) and Warth *et al.*, (1997); which are carried out at higher temperatures to 250 Celsius degrees, where is possible decomposition of the oil and undesirable by-products. Wang *et al.* (2008) obtains biodegradable foams from maleated castor oil (MACO), obtained by esterification of hydroxyls using maleic anhydride in a temperature range from 80 to 120 Celsius degrees. The mechanism of addition of nucleophiles to reactive carbonyl compounds is a subject of continuing interest (Andrés and de Rossi, 2005; Skrzypek *et al.*, 1998).

In this work we have proposed study the kinetics of this reaction without condensation, determine some thermodynamics and kinetics parameters through mathematical modeling and validated the model obtained with experimental data.

II. METHODS

A. Materials

Castor oil, grade USP, with a OHv value equal to 159.51 mg of KOH/g of sample, maleic anhydride, commercial grade.