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A Transesterification Double Step Process — TDSP for biodiesel preparation from fatty acids triglycerides

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ABSTRACT

This study introduces a two consecutive steps basic–acid transesterification process, (denominated Transesterification Double Step Process — TDSP) for biodiesel production from vegetable oils. The process involves homogeneous consecutive basic–acid catalysis steps and is characterized by formation of well-defined phases, easy separation procedures, high reaction velocity and high conversion efficiency. The proposed TDSP is different in relation to other traditional two-step procedures which normally include acid esterification followed by basic transesterification, or enzymatic or even supercritical transesterification conditions. The biodiesel (fatty acid methyl esters) was analyzed by standard biodiesel techniques in addition to ^{1}H-NMR, indicating high quality and purity biodiesel products. The transesterification of sunflower and linseed oils resulted in oil conversions higher than 97% corresponding to yields of 85%. A probable reaction mechanism responsible for the process is presented.

1. Introduction

Approximately 100 years after the initial experiences of Rudolph Diesel, the international community with new chemical knowledge, evaluates the possibility to obtain biofuels, similar to the Diesel fuel, as well as, other products from the chemical treatment of triglycerides (vegetable or animal fats and oils). This development is based on the knowledge of catalytic processes as well as the evolution of instrumental techniques, which permitted the elucidation of the esterification mechanisms and consequently the study of transesterification. Homogeneous and heterogeneous processes were studied focusing on basic, acid and enzymatic catalysis [1–18].

Usually, two-step procedures were used to prepare biodiesel from different oils, which have high content of free fatty acids [19–26]. In these works the first step is the acid catalyzed esterification, which reduces the free fatty acids (FFA) content of the oil and minimizes the soap formation in the second step (basic catalyzed transesterification). Other papers reported the biodiesel production by two-step process using supercritical conditions [27–31], as well as employment of enzymes [32–34]. The present work presents a new two-step procedure based on the combination of consecutive basic and acid catalysis. Therefore, there is no initial acid attack and acid esterification stage for elimination of free fatty acids as proposed by other papers. Additionally, as it is going to be shown, the second step is not a simple neutralization, but constitutes a catalytic stage.

1.1. Transesterification

The ideal transesterification with a primary alcohol is given by the overall reaction, Fig. 1. The main feature of this reaction is the transformation of the triglyceride to glycerol and three ester molecules. These esters constitute the components of the biodiesel. The reaction includes at least a catalytic component.

In reality the transesterification process never occurs in the ideal form. A better approximation is given by the scheme Fig. 2 where the chemical agents and products are present without consideration of stoichiometric parameters. So, after finishing the reaction, we must count with the presence of triglycerides, diglycerides, monoglycerides, biodiesel esters, glycerol, alcohol, and catalytic components and in the case of basic catalysis, soap moieties. In the literature, there is no evidence of transesterification with 100% conversion efficiency. Normally the basic catalysis presents conversions of approximately 82%, however the acid catalysis provides higher conversions, approximately of 98% but the process is extremely slow [1–3,6–8].

1.2. Catalytic processes

In this part some aspects of the advantages and disadvantages of acid and basic catalysis are presented. This discussion is important in order to elucidate the new transesterification procedure and the mechanism proposed in this work.

1.2.1. Acid catalysis

The acid catalysis transesterification includes the combination of three reversible reactions (Fig. 3). The high conversion of the acid

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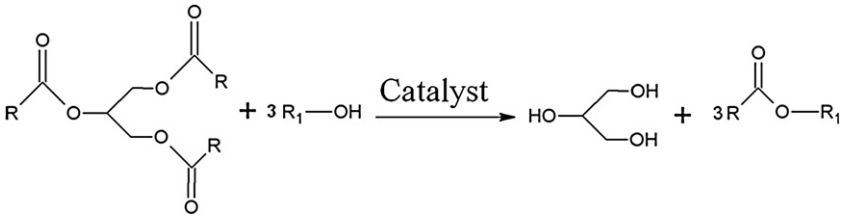

Fig. 1. Ideal process of transesterification.

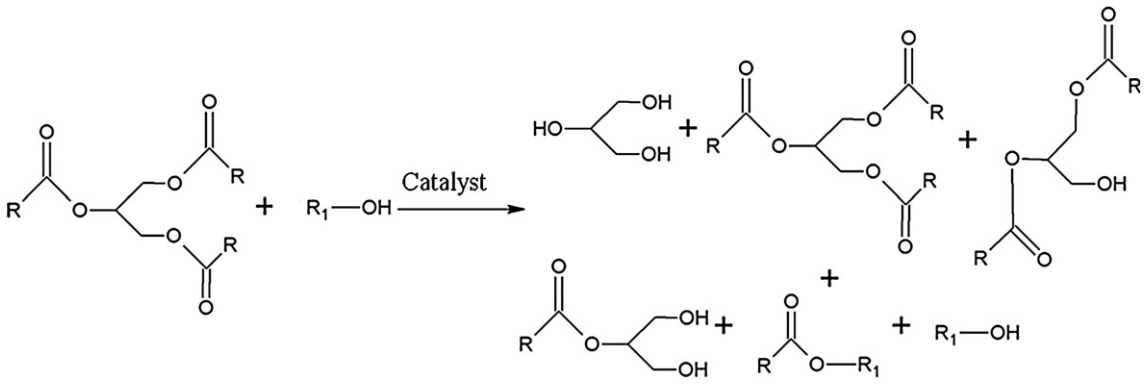

Fig. 2. Real transesterification process.

catalyzed transesterification procedure is due to capacity to transesterify fatty acids and fatty acid salts present in the system. The employed acids are HCl, H_2SO_4, BF_3 and sulfonic acids [1–3,14]. However, it is generally accepted, that the acid catalysis is many times slower than the basic. The velocity of the biodiesel production reaction with acid catalyst is related to the conditions of the transesterification reaction. We mention the alcohol/triglyceride molar ratio, the temperature, the concentration of catalyst, the purity of reactants which affect velocity and chemical equilibrium [1,4–7]. The alcohols used in this process are methanol, ethanol, propanol, butanol (n, s, and t) and amyl alcohol [1]. The alcohol/triglyceride molar ratio is essentially large; generally, the best one is approximately 12 alcohol molecules for 1 triglyceride molecule. The excess is used in order to shift the reaction equilibrium, to avoid the reverse reactions and to accelerate the process [1,5,7]. The temperature influences the velocity of the electrophilic attack; this way affects the yields and consequently decreases production cost [1,5,6]. The concentration of catalyst is directly related to the yields; in excess the one promotes reverse reactions, while a low catalyst concentration results in a limited process evolution [4,6,8,13]. The impurities promote parallel reactions, however higher temperature and pressure can eliminate this influence, but yields cannot be optimized [4].

1.2.2. Basic catalysis

The basic catalysis is the industrially more used transesterification process. It presents many advantages as a fast reaction with low alcohol/triglyceride molar ratio and good yields [5,14]. However the basic catalysis requires more rigid anhydrous conditions than the acid. The presence of water leads to irreversible hydrolysis of lipids [3–6,9]. It can form emulsion or soap if the catalyst concentration is higher than the necessary one. Essentially the species used in this process are potassium hydroxide, sodium hydroxide, and generally Lewis bases, except the oxides that form heterogeneous systems. According to Fig. 4, it is observed the formation of the active species, with similar manner to the alkoxides. The active species attack the carbonyl moiety in triglyceride, originating a tetrahedral intermediate, from which the alkyl ester and the corresponding anion of the diglyceride are formed [12,16,17]. Regeneration of the active species occurs after the liberation of the mono alkyl ester. The formation of the glycerol occurs in the finishing of the process. Normally a small excess of the alcohol is necessary in order to dislocate the equilibrium to the products and to avoid parallel reactions [5]. The reaction time decreases significantly by using temperatures near the boiling point of the alcohol [4,5].

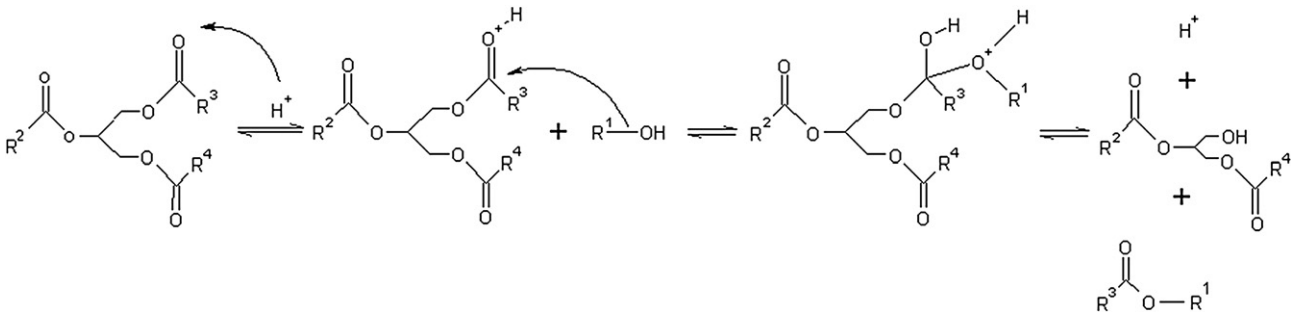

Fig. 3. Mechanism of transesterification according to acid catalysis.