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## Castor oil preheater selection based on entropy generation and exergy effectiveness criteria

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### ABSTRACT

Castor oil has an especial hydroxyl fatty acid (*cis*-12-hydroxyoctadeca-9-enoic acid) which provides unique properties and unusual versatility as a raw material for biodiesel production. Heating and pumping are the major energy demanding in biodiesel production processes. Biodiesel production may not be competitive among the liquid renewable fuels unless the elevated energy consumption is reduced. Actually, this problem is more pronounced in Castor oil biodiesel industry. In this work, the problematic of the elevated power consumption in the pumping system was solved by preheating the Castor oil. The additional heat reduces the viscosity, as well as, the activation energy in the reactor leading to a smaller residence time. The preheater device has been designed based on exergy effectiveness transfer and dimensionless entropy generation approaches which are highly related with energy efficiency. The performed study compared parallel, crossflow, Shell-and-Tube, and countercurrent flow arrangements. A 6-3 Shell-and-Tube heat exchanger obtained the highest performance in terms of exergy effectiveness transfer and dimensionless entropy generation. The thermodynamic property calculations were performed by using a thermodynamical model based on molecular theory (SAFT –  $\gamma$ ). These calculation are required for the rigorous heat exchanger design. Eight of the most common Free Fatty Acids presented in Castor oil were integrated in the oil mixture.

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### 1. Introduction

Biodiesel is considered as an alternative for diesel fossil fuel. It is obtained from vegetable oils or lipids through alcohol reactions. Biodiesel is nontoxic, biodegradable, environmentally friendly, and considered as a renewable energy sources that contributes to greenhouse gas reduction [1]. Biodiesel production mostly consists of a chemical reaction between vegetable or animal oil with alcohol as methanol. Conventional production processes refer to transesterification procedures which oils and alcohols react in liquid phase in the presence of a base catalyst (usually sodium hydroxide). These processes have a fatty acid feedstock at room temperature that is conducted to chemical reactor or a mixer (where it is blended

with a methanol stream) by a pump. There are different potential sources to obtain biodiesel such as fats and oils edible and non-edible, that can be used as raw material [2]. Castor oil, also known as Ricinus oil, is a Free Fatty Acid (FFA) mixture within the seed of the castor plant, *Ricinus communis* L. Castor oil, rich in a very unique Hydroxyl Free Fatty Acid (HFFA), ricinoleic acid  $C_{18}H_{34}O_3$  structurally known as *cis*-12-hydroxyoctadeca-9-enoic acid, a 18 carbon hydroxylated fatty acid having one double bond. The presence of ricinoleic acid provides castor oil its unique properties and unusual versatility [3]. Despite this, castor oil has the higher viscosity than other commercial fatty acid sources [4]. Biodiesel production from Ricinus oil has been identified as an important potential raw material for the local production of biodiesel in several places around the world, as well as, it has become a booming business [5,6]. Castor oil biodiesel is lower cost in comparison to vegetable oils [1]. Nevertheless, high viscosity of the methyl ester from ricinoleic acid, exceeds the maximum value for

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kinematic viscosity in both ASTM D6751 and EN14214 biodiesel standards [7]. In addition, ricinoleic acid has higher viscosity than the produced methyl ester through it. Biodiesel production has some drawbacks. Despite efforts to reduce energy costs, they are still high (around 0.53 USD per liter [8]). Energy consumption is one of the most important challenges for biodiesel industry [9]. Unless biodiesel industry can reduce the elevated energy demand, probably biodiesel will not be competitive and therefore this problem is more pronounced for castor oil biodiesel industry. In order to reduce energy costs, the viscosity of the castor oil should be reduced by means of heating the stream entering the reactor. Additionally, higher conversion can be achieved by increasing the reaction temperature and the reaction time. Moreover, the heating load in the reactor will be less [10]. For industrial biodiesel processes, there are different ways to design a biodiesel production process independently of its raw materials [11]. West et al. [12] have designed four processes to convert a waste vegetable oil feedstock into biodiesel. They integrate the bottom distillation column stream with a heat exchanger to preheat the raw materials. The first two processes use pre-treated alkali and acid catalysts; the others employed a heterogeneous acid catalyst and a supercritical method. For reducing costs, a preheater can aid to reduce viscosity and pump load before to be taken to the reactor. The preheater design requires thermodynamic properties data for the hot and cold fluid, as well as, for the heat transfer coefficient calculations and then the heat exchanger geometrical parameters [13]. The literature on thermodynamic properties prediction for castor oil is limited on group contribution empirical models where a big amount of data for fatty acids like-molecules is fitted and extended for other similar molecules [14–16]. Huber et al. [17] have developed an equation of state (EoS) for soy bean biodiesel using experimental data and thermodynamic theory. Molecular theories for FAs and their Fatty Acid Methyl Esteres (FAMES) have been studied by Olivera et al. [18] comparing predictions between common cubic EoS and associating cubic EoS. Perdomo et al. [19] have developed a thermodynamical model for any FFA, FAME and Fatty Acid Ethyl Ester (FAEE) and their mixtures are based on the modification of the statistical association fluid theory called SAFT –  $\gamma$  [20,21]. This work uses the SAFT –  $\gamma$  approach in order to predict the thermophysical properties of Castor oil.

Thermal design and optimization methods have been widely used for the study of thermal systems emphasizing engineering economics, system simulation, and optimization methods [22]. The methods of exergy analysis, entropy generation minimization, and thermoeconomics are the most used strategies to design thermal equipments with high energy efficiency. In this work, the performance of different kinds of preheaters for a castor oil biodiesel production are analyzed using a second law analysis and an exergetic criteria. The analysis and design of heat exchangers requires the evaluation of the entropy generation and/or exergy destruction due to heat exchange and pressure drop as a function of the design variables [23]. The first proposal presented by West, in Ref. [12], is adapted to industrial conditions referred by Santana et al. [24] analyzing heat exchanger performance for castor oil biodiesel plant where it works as a preheater then castor oil requires heating with the aim of reduce viscosity and pumping load. In this work, several heat exchanger flow configurations have been evaluated in order to obtain the most appropriated one for the castor oil preheater.

## 2. Preheater performance and selection

Heat exchangers, one of the most common devices in industry, are used to move energy from one fluid to another [13].

An adequate use of heat exchangers considers their design, thermal performance improvement, and size–weight reduction [25]. The heat exchanger effectiveness number of transfer units method ( $NTU - \epsilon$ ) is used to design heat exchangers as well as to check performance in operating installed devices [26]. In this method, the terms  $NTU$  and  $\epsilon$  are interpreted as the relative quantity of the heat transfer rate compared to the enthalpy change rate of the fluid with smaller heat capacity and the measure of thermal performance of a heat exchanger, respectively [27]. Table 1 summarizes different effectiveness expression for heat exchangers here analyzed.

### 2.1. Modeling castor oil thermophysical properties

Castor oil is a fatty acid mixture which is principally conformed by Ricinoleic acid. Table 2 shows the average composition of castor oil. Castor oil is a highly non-ideal fluid and its thermophysical properties are not well estimated yet, especially second derivative properties like heat capacity, speed of sound, etc. Perdomo et al. [19] have proposed a model based on a version of the statistical association fluid theory called SAFT –  $\gamma$  [20,21] to represent thermodynamical properties for FFAs and Fatty Acid Alkyl Esters (FAAEs). Same author model has shown to be versatile for different kinds of fatty acid alkyl ester mixtures and for any combination of them [28] due to its group contribution formulation. In this work, we have used this approach to model castor oil as a mixture of the fatty acids profile shown in Table 2, extracted from Ref. [29]. As it was mentioned above, Castor oil is a mixture (HFFA/FFA) of HFFA (Ricinoleic Acid and Dihydroxystearic acid) and commons FFA (Linoleic, Oleic, Stearic, Palmitic, Eicosanoic and Linolenic acid). Their molecular structures are very important in order to be modeled by SAFT –  $\gamma$  approach [28].

SAFT –  $\gamma$  EoS is presented in terms of four molecular contributions:

$$\frac{A}{NkT} = \frac{A^{IDEAL}}{NkT} + \frac{A^{MONO}}{NkT} + \frac{A^{CHAIN}}{NkT} + \frac{A^{ASSOC}}{NkT}, \quad (1)$$

where  $N$  is the number of chain molecules in the mixture,  $k$  is the Boltzmann constant and  $T$  is the temperature. Now,  $A^{IDEAL}$  is the ideal free energy,  $A^{MONO}$  is the residual free energy due to the monomer segments,  $A^{CHAIN}$  is the contribution due to the bonding of monomers required to form a chain molecule and  $A^{ASSOC}$  describes the contribution to the free energy due to intermolecular association, which in this case are represented by hydrogen-bonding between carbonyl and hydroxyl groups. The energy contributions per molecule are functions of the energies per segment and, as well as the total number of segments that comprise the respective  $i$  molecular specie in the system expressed by:

$$NS = \sum_{k=1}^{NG} \nu_{k,i} \nu_k^* s_k, \quad (2)$$

where  $s_k$  corresponds to the proportion of each spherical segment in group  $k$  that contributes to the overall properties of the molecule, and  $NG$  is the number of chemical groups present in molecule  $i$ . Hydroxylated fatty acids contain a type  $b$  site (partial positive charged hydrogen atom in the hydroxyl group), two type  $a$  in the hydroxyl group and, additionally, the same number and types of sites already considered in FAs. Notice that HFFA can associate either with other FFAs or with itself. The Helmholtz free energy contribution due to association is given by Ref. [21]:

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