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Hydrotreatment of sunflower oil using supported molybdenum carbide

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ABSTRACT

Pure sunflower oil was hydrotreated ($T = 633$ K, $P = 5$ MPa) aiming the production of a biofuel in the diesel range using β-Mo_2C/Al_2O_3 as catalyst. The catalyst was synthesized in situ using the temperature-programmed carburization (TPC) methodology with a 20% (v/v) CH_4/H_2 gas mixture and 923 K/2 h as synthesis temperature. The catalytic evaluation results indicate that for the employed conditions n-C_{18} was the major product. The association of the results of the experiments without (blank) and with catalyst suggests that the overall triglyceride transformation into linear alkanes proceeds in two steps: (i) thermal cracking of the triglyceride forming free fatty acids and (ii) hydrogenation of the double bonds and of the carboxylic group of the free fatty acid forming n-alkanes. No CO and/or CO_2 formation were detected implying that decarbonylation and/or decarboxylation routes do not play an important role when molybdenum carbide is used, contrarily to what is commonly observed when supported Co–Mo or Ni–Mo sulfides are employed as catalysts.

1. Introduction

In addition to the growing concerns regarding the increased consumption of oil products, natural gas and coal to generate all of the energy required primarily by the industrial and transportation sectors, additional concerns have arisen with respect to environmental issues, which has resulted in the creation of stricter laws worldwide. The increase in CO_2 emissions from the burning of oil and coal is currently the major international concern because it allegedly contributes significantly to the greenhouse effect. In this sense, the search for alternative sources of renewable energy with minimum emissions is necessary.

Biodiesel is produced from the process of transesterification of triglycerides (vegetable oils or fats) and has been used in several countries in its pure form or mixed with petroleum diesel. The major disadvantage of this process is related to the production of large amounts of glycerol, which has significantly impacted the market of this product. If this process is effectively implemented in large countries, such as Brazil, the United States and China, or in economic regions, such as the European Community, the supply of glycerol will be so high that experts predict that there will be a collapse in the market for this product.

Several studies available in the literature show that the hydrotreating (HDT) process employed in refineries around the world can be used to obtain hydrocarbons in the range of diesel and gasoline from pure vegetable oils or from mixtures of vegetable oil and diesel using the conventional catalytic HDT technology and commercially available catalysts [1–11].

The vast majority of studies dealing with the processing of vegetable oils by hydrotreating have utilized the $NiMo/Al_2O_3$ sulfide catalyst [1–10]. However, studies exploring the use of $CoMo/Al_2O_3$ [11–14], Pt deposited on various supports [15–18], Pd/SAPO-31 [19], commercial hydrocracking catalysts [15,17,19,20], $NiMoW/Al_2O_3$ [21,22] as well as the use of CoMo and NiMo sulfide phases on supports such as SiO_2 [14,18], MCM-41 [4,23] and zeolites [7,9,11,13,14,18] have also been reported.

If from one side the used of sulfide catalysts in the co-processing of vegetable oils and refinery streams is advantageous because the existing infrastructure can be used without too many modifications, from the other it is not convenient for the processing of streams of pure vegetable oil unless some sulfur is added to them in order to keep the catalysts in its active form. In fact Kubička and Horáček [14] have shown that when a $CoMo/Al_2O_3$ sulfide catalyst was used for prolonged periods of time it underwent deactivation due to the loss of sulfur from the active phase. Therefore, the addition of a sulfiding agent to the pure vegetable oil to be processed, such as CS_2 or dimethyl disulfide (DMDS), is necessary to minimize catalyst deactivation. However, the addition of sulfiding agents to

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