Fuel 117 (2014) 1010–1019

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Physico-chemical properties and thermal degradation studies of commercial oils in nitrogen atmosphere

Vikranth Volli, M.K. Purkait *

Indian Institute of Technology Guwahati, Guwahati 781039, Assam, India

HIGHLIGHTS

- Thermal degradation of various commercial oils has been investigated in N_2 atmosphere.
- Activation energy of oils calculated in N_2 atmosphere was quite less than that of in air oxidation.
- It was observed that free fatty acid content in non-edible oils were more than edible oils.
- The order of activation energy was observed as: karanja > soybean > mustard > olive.

ARTICLE INFO

Article history:
Received 18 March 2013
Received in revised form 10 October 2013
Accepted 10 October 2013
Available online 23 October 2013

Keywords:
Commercial oils
Thermogravimetric analysis
Iso-conversional method
Activation energy
Flash point

ABSTRACT

Thermal properties and reaction kinetics of commercial oils play prominent role in design, operation and modeling of systems with various industrial applications including cosmetics, lubrication, fuel and food processing. In the present work, thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG) techniques were used to study the thermo-chemical behavior of four varieties of oils (mustard, soybean, olive and karanja). The thermal degradation was studied in an inert (N_2) atmosphere from ambient temperature to a temperature of 600 °C using a heating rate of 10, 20, 30, 50, 100 °C min^{-1}. The chemical composition and thermal properties were investigated by measuring FTIR, DSC, CHNS and ^1H NMR. Physical properties such as moisture content, viscosity, ash content, flash, fire, pour and cloud points were also determined. The model-free iso-conversional methods were used to determine kinetic parameters without making any assumptions about the reaction function and reaction order which avoids the risk of obtaining wrong kinetic parameters, especially activation energy, due to pre-assumption of inappropriate reaction function. Four degradation models including modified Coats and Redfern, Friedman, Kissinger and Flynn–Wall–Ozawa methods were used to determine the apparent activation energy.

1. Introduction

India is one of the largest producers of commercial edible and non-edible oils with oil seeds are the major sources. About 90% of the vegetable oils produced from these sources are used for edible purpose and the rest are used for varieties of industrial applications. The depletion of petroleum resources lead to an energy crisis and as an alternative, the use of these commercial edible and non-edible oils has been proposed as a raw material in bio-diesel production. The use of these oils poses a great challenge to the scientific community because these are triglycerides (polyunsaturated, monounsaturated and saturated fatty acids) and tend to decompose or oxidize under conventional processing conditions. High viscosities of these oils cause durability problems along with poor atomization pattern when used as fuel [1]. Comprehensive knowledge regarding the thermal degradation of oils might result in development and establishment of technologies for various industrial applications.

The use of thermo-analytical techniques such as thermogravimetric analysis (TGA), differential thermogravimetric analysis (DTG) and differential scanning calorimetry (DSC) of oils has gained a lot of importance in recent times. Santos et al. [1] evaluated the decomposition kinetics and thermal stability of eight samples of commercial edible oils in air atmosphere at heating rate of 2, 5, 10 and 20 °C min^{-1}. Integral and approximation methods were used to determine kinetic parameters. The order of stability was determined to be corn > sunflower > soybean > rice > soybean + olive > sunflower + olive > canola > olive. The effects of alpha-tocopherol (vitamin E) on thermal stability and the thermal degradation behavior of sunflower, soybean oil and their blend in air atmosphere at 5, 10 and 20 °C min^{-1} heating rates were studied by Sanjiv et al. [2]. The sequence of thermal stability was found to be as (sunflower + soybean) > sunflower > soybean. Souza et al. [3]

* Corresponding author. Tel.: +91 361 2582262; fax: +91 361 2582291.
E-mail address: mihir@iitg.ernet.in (M.K. Purkait).

0016-2361/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.fuel.2013.10.021

evaluated the thermo analytic and kinetic parameters of sunflower oil with and without oxidants in air atmosphere at 5, 10 and 20 °C min^{-1} heating rates. Deterioration of sunflower oil under frying conditions were also studied using DSC and non-isothermal thermogravimetry in both air and nitrogen atmosphere. Vecchio et al. [4] studied the thermoxidation of 12 varieties of olive oils by simultaneous TGA and DSC in air atmosphere at heating rates of 2.5, 5, 7.5 and 10 °C min^{-1}. The use of DSC to determine the iodine value (IV) of palm oil and its products was studied by Haryati et al. [5]. The DSC analysis showed a clear separation of the substances that have low and high melting points

Tan and Che Man [6] examined the thermal degradation profiles of 17 edible oils by DSC. Melting and crystallization curves of all the samples were reported. It was found that the oil samples with a high degree of saturation (IV < 65) showed DSC melting and crystallization profiles at higher temperature regions than the oil samples with high degree of unsaturation (IV > 65). Souza et al. [7] studied the thermal and kinetic behavior of methanol biodiesel derived from cotton oil. Non isothermal dynamic analysis method in both air and nitrogen atmosphere was used at heating rate of 10 °C min^{-1}. It was found that the activation energy of cotton seed oil was higher than its biodiesel. Studies on the oxidative kinetics of soybean oil/anhydrous milk fat blends by DSC at heating rate of 2.5, 5, 7.5, 10 and 12.5 °C min^{-1} were done by Thurgood et al. [8]. Arrhenius parameters were calculated by using Flynn–Wall–Ozawa method. It was reported that the activation energy varied from 58.5 to 117.4 KJ kg^{-1}. Jain and Sharma [9] studied the thermo oxidative behavior of jatropacurcas biodiesel with and without oxidant. Direct Arrhenius plot method was used to determine the kinetic parameters in air at 10 °C min^{-1} heating rate. Pyrogallol was found to have significant effect on onset temperature of biodiesel.

From the above literatures it may be depicted that the thermal degradation studies of commercials oils like soybean, sunflower, olive, corn, canola and rice bran are investigated in presence of air. However, to the best of knowledge of authors, thermal degradation studies in nitrogen atmosphere have not been studied. Again, thermal degradation of Mustard and Karanja oil has not been studied yet. Moreover, various models have been used to compute the kinetic parameters and the use of single heating rate in calculation of activation energy (E_a) gives unreliable result. Present work focused on the degradation studies of various commercial edible and non-edible oils including mustard and karanja oil in nitrogen atmosphere and adoption of more simplified and an accurate method to determine the activation energy (E_a).

The current study deals with the thermal degradation behavior of commercial oils along with the determination of activation energy using model-free iso-conversional methods. Four degradation models including modified Coats and Redfern, Friedman, Kissinger and Flynn–Wall–Ozawa methods were used. These methods calculate the reaction activation energy (E_a) without making any modelistic assumptions and hence accurate results were obtained. Physical properties such as moisture content, viscosity, specific gravity, acid value, calorific value, refractive index, ash content, flash, fire, pour and cloud points were also determined. The chemical composition and thermal properties were investigated by using Fourier transform infrared spectroscopic (FTIR), differential scanning calorimetric (DSC), proton nuclear magnetic resonance (^{1}H NMR) and ultimate analysis.

2. Experimental

2.1. Materials

Ten samples of commercial edible (sesame, palm, refined soybean, mustard and sunflower) and non-edible (neem, olive, mahua, castor and karanja) oils were purchased from several local retailers, Guwahati, India. Various physical and chemical properties were measured for all the oils. Details of measurement procedures are explained below.

2.2. Measurement of physical properties

Various fuel properties such as moisture content, viscosity, density and flash point of oils are known to be the typical key properties for combustion in boiler, furnace and engines. The pH values of all the samples were measured by using pH Spear from Eutech instruments. The volumetric Karl Fischer technique was used to determine the water content in the samples. In this study, a Titrino 787 Karl Fischer from Metrohm was used. The reagents used (hydranal solvent oil and hydranal titrant 2) were purchased from Sigma–Aldrich, India. Specific gravity of all the samples was measured at room temperature using specific gravity bottle as per American society for testing and materials (ASTM) D 1298-85. The viscosities of the samples were measured using rheometer (Rehostress RS 1) from Thermo Electron according to ASTM D 445. All viscosity measurements were obtained at 40 °C using the in-built temperature controller. Flash and fire points were obtained by using Cleveland open cup apparatus as per ASTM D 93-90. Cloud and pour point determinations were performed according to ASTM D 2500, 97 using RW 2025 G JIEO Tech from Lab companion. Acid value was determined as per ASTM D664-89. The refractive index was measured using ATAGO DR A1 refractometer from ABBE. Calorific values of the samples were measured by using bomb calorimeter according to ASTM D 240-92. Ash content of the samples was determined by ASTM D 482-91.

2.3. Measurement of chemical properties

Thermogravimetric analysis (TGA) was done by using Mettler Toledo TGA/SDTA 851^e with nitrogen as carrier gas at a constant flow rate of 45 ml min^{-1}. The sample weighing 11 mg was heated from an initial temperature of 25–600 °C at a heating rate of 10, 20, 30, 50 and 100 °C min^{-1}. A Mettler Toledo DSC-1 STAR^e with refrigerated cooling system operating within a temperature range from 25 to 450 °C was used to measure the heat requirement of the samples. The experiments were performed under atmospheric pressure and with nitrogen supplied at 45 ml min^{-1}. The DSC was calibrated regularly with alumina as reference material. The obtained DSC curves give the heat flux (mW mg^{-1}) in function of the temperature or in function of the time (constant heating rate 10 °C min^{-1}).

Various characteristic functional groups present in each oils were identified by using SIMADZU CORP Fourier Transform Infrared spectroscopy (FTIR). On interaction of an infrared light with materials, chemical bond will stretch, contract and absorb infrared radiation in a specific wave length range regardless structure of the rest of the molecules. The FTIR spectra were collected in the range of 400–4000 cm^{-1} region with 8 cm^{-1} resolution. The raw materials were analyzed to determine the amounts of carbon, nitrogen, hydrogen, sulfur and oxygen (calculated from difference) by elemental CHNS (carbon, hydrogen, nitrogen and sulphur) analyzer according to ASTM D5291-96. ^{1}H NMR analyses were performed at 298 K on a Varian DRX – 400 spectrometer using 5 mm broad band probe head with a z-gradient. The spectra were obtained at 400 MHz for ^{1}H, using dimethyl sulphoxide (DMSO) D6 as the solvent and trimethyl silane (TMS) as the internal standard. For each determination, 10 μL of the pure sample were dissolved in 40 μL of DMSO.