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Thermal and flow properties of fish oil blends with bunker fuel oil

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HIGHLIGHTS

- Bio-oil blends with RFO potential for domestic/regional application have been studied.
- Some important properties of crude bio-oils, RFO and their blends have been analyzed.
- Flow barrier decreased with increasing concentration of fish oil in blends with RFO.
- High concentration of crude bio-oils in blend with RFO exhibits good flow properties.

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ABSTRACT

The thermal, flow, and heating properties of unrefined fish oils (anchovy–sardine oil derived from fish processing waste, and unrefined salmon oil derived from salmon discards) blended with bunker 'A' oil (a common heating oil) were investigated. The rheological properties of the blends were examined and modeled using an Arrhenius equation approach. The onset of thermal degradation of waste fish oil, salmon oil and bunker 'A' oil were 187 °C, 229 °C and 75 °C respectively and complete decomposition of the oils occurred between 500 and 550 °C. The flow behavior index of the oil/blend samples was less than one, which indicated that the fish oil/blend exhibited non-Newtonian fluid behavior. More so, all samples showed decreasing viscosity with increasing shear rate indicated that the samples and their blends exhibited a shear-thinning non-Newtonian behavior. The average heating value of anchovy–sardine oil, unrefined salmon oil and bunker fuel oil were 38.69, 39.51 and 43.36 MJ kg^{-1} respectively. The energy barrier to flow and viscosity of the blends decreased with increasing quantity of fish oils in fish-bunker mixture.

1. Introduction

Fish processing facilities generate a significant amount of fish by-products that could be source of energy, food, or industrial chemicals. While fish oil is a natural source of omega-3 polyunsaturated fatty acids (mostly eicosapentaenoic acid (EPA), and docosahexaenoic acid (DHA)) used in nutritional supplements, monetizing these oils may be challenging at processing facilities where there is limited infrastructure and plants are remotely located. Under these conditions, extraction of oil from fish by-product for use as an in-house or regional fuel may be both economically and environmentally more sustainable approach. Processes to extract and refine fish oil for fuel are less energy intensive than those used for nutritional quality oil extraction/refining due to higher product quality standards required to meet nutritional regulations. Further, extraction of oil from waste (fish residue) for biofuels does not negatively impact food production [1].

Biofuels are gaining more attention due to availability, renewability and other advantages such as, net greenhouse gas (GHG) reduction, improved combustion, biodegradability and low toxicity [2]. Studies have proposed using fish oil and/or blending with petroleum based fuels as an alternative fuel oil for convectional combustors or diesel engines [3,4]. Fish oil has been used as fuel oil in power/heat generation as these systems can tolerate lower fuel quality than diesel engines [4]. Bunker fuel oils (Nos. 2 to 6) [5,6] are heavy petroleum distillates and are viscous, lower-grade fuel oil used to produce electricity, to fire boilers and blast furnaces in industry (notably the pulp and paper industry), and to power large marine and other vessels. Bunker fuels contain sulphur resulting in sulphur dioxide and as well as other contaminant emissions (due to the high molecular weight of the fuel) [7]. Blending fuel oils with unrefined fish oils could reduce emissions

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Nomenclature

A	frequency factor (Pa s)
B100	100% biodiesel
CO	carbon monoxide emission
DHA	docosahexaenoic acid
DSC	differential scanning calorimeter
Ea	activation energy (kJ mol^{-1})
EPA	eicosapentaenoic acid
GHG	Greenhouse gas
HHV	higher heating values (MJ/kg)
K	consistency index (Pa s^n)
k	reaction rate constant
MUFA	monounsaturated
n	flow behavior index (dimensionless unit)
OCN	ocean nutrition Canada
PUFA	polyunsaturated fatty acid
R	gas constant (8.314 J mol^{-1} K^{-1})
RFO	residual fuel oil (bunker fuel oil)
SB20	20% (v/v) unrefined salmon oil in 80% (v/v) bunker fuel oil
SB50	50% (v/v) unrefined salmon oil in 50% (v/v) bunker fuel oil
SB80	80% (v/v) unrefined salmon oil in 20% (v/v) bunker fuel oil
SFA	saturated fatty acid
SSE	sum of square errors
T	temperature (K)
TGA	thermogravimetric analysis
WB20	20% (v/v) waste fish oil in 80% (v/v) bunker fuel oil
WB50	50% (v/v) waste fish oil in 50% (v/v) bunker fuel oil
WB80	80% (v/v) waste fish oil in 20% (v/v) bunker fuel oil
ΔH	enthalpy (kJ/kg)
τ	shear stress (Pa s)
γ	shear rate (s^{-1})
ω-3	omega-3

associated with this equipment particularly sulphur dioxide. An investigation by Preto et al. [4] reported that fish oil blends with Nos. 6 and 2 fuel oils burn well in conventional furnaces resulting in lower overall pollutant emission. The fish oil also reduced the viscosity of the fuels through blending [3]. While this work is promising, in order to use blends of fish oil and petroleum effectively, knowledge of thermal stability, rheological properties, enthalpy and other cold flow properties of the blends is required. There is limited literature on the properties of heavy oil-fish oil blends. A comparison of the quality of fish oil compared to the petroleum based fuels was done using thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) among other methods [8–10]. Operations related to the mass transfer and liquid flow, such as pumping, storage and handling, are addressed with rheological knowledge of the fluid [8]. There are few published studies on the thermal stability and rheological properties of fish oil [8–10] and less on blends of fish oil and/waste fish oils with heavy petroleum oils.

The objective of this work is to evaluate thermal stability, rheological, and heating value, of unrefined salmon oil, waste fish oil, and blends with bunker fuel oil.

2. Materials and methods

2.1. Sample preparation

Fresh salmon waste (head, gut, trimming and frame) were obtained from the Centre for Aquaculture and Seafood Development (CASD), Memorial University of Newfoundland (MUN). The waste was stored at −40 °C. As part of the oil removal process, the waste was thawed, ground to 1–4 mm and heated in a hot water bath at 80 °C for 10 to 15 min. The heated waste was transferred into eight 50 mL centrifuge tubes and centrifuged in an Eppendorf centrifuge 5810 (Eppendorf AG 22331, Hamburg-Germany) at 3850 rpm for 9 min. The fish oil was separated by decantation and stored again at −40 °C. The same oil recovery method was used to recover oil from Atlantic Cod, herring and mackerel. Bunker fuel oil and waste fish oil were supplied by St. Francis Xavier University, Nova Scotia. The waste fish oil is a by-product of Ocean Nutrition Canada Ltd. (ONC). Omega-3 fatty acids are extracted/concentrated from anchovy (95–99%) and sardine (1–5%) oil imported from Peru, off coast of South America. The waste fish oil 'as is' was stored in the freezer at −40 °C until used while the bunker fuel oil kept in cold room at temperature between 0 and 4 °C.

2.2. Thermo gravimetric analysis (TGA)

The thermal stability of the unrefined salmon oil, and waste fish oil and their blends with the bunker fuel was conducted using the Thermo-gravimetric Analyzer (Model Q500, TA Instruments Inc.). Approximately 0.8–1.2 mg of oil/blend sample was loaded into the furnace. The TA instrument was manually programmed to heat up the sample from ambient temperature condition to 800 °C under N_2/air atmosphere at the ramping rate of 5 °C/min. Sample weight change was automatically acquired every second and the data were analyzed and plotted using the TA Universal Analyzer Software.

2.3. Calorific value/high heating value (HHV)

The calorific value of a fuel is the thermal energy liberated per unit mass of fuel during a complete combustion reaction till the products of combustion are cooled back to the initial temperature of the combustible materials [11]. Calorific value is a measure of the energy content in a fuel. The 1108 oxygen bomb calorimeter (Parr Instrument Company) was used to determine the HHV of the unrefined salmon and waste fish oils and the blends of each with bunker fuel oil according to ASTM D2015 standard method [31]. Oxygen – bomb vessel was pressurized to approximately 3 MPa with an oxygen container. The bomb was ignited automatically after the jacket and a bucket temperature equilibrates to the desired values.

2.4. Flash point testing

The flash point of a fuel oil is the lowest temperature, corrected to atmospheric pressure, at which application of a naked/test flame cause the fuel-vapor to ignite under specific conditions of test [11]. The flash point of the oils and their blends were measured by Pensky-Martens closed cup apparatus (K16200 – Koehler Instrument Company Inc.). The flashpoints were determined in accordance with ASTM D93 [30]. The apparatus is equipped with closed cup to which sample is fed and heated at a controlled rate. An ignition source was introduced and the temperature at which the heated oil flashes was recorded as the flash point.

2.5. Melting points and enthalpy

Melting points were determined in a METTLER TOLEDO DSC-1 (Differential Scanning Calorimeter) with Julabo intercooler and