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Comparison of biofuel quality of waste derived oils as a function of oil extraction methods

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HIGHLIGHTS

- Fuel oil qualities of salmon waste-derived bio-oil have been studied.
- Bio-oil qualities are highly depend on the extraction methods.
- SC-CO_2 oil is of high quality for fuel use or biofuel feedstock.
- Oil impurity level determines the bio-oil flow properties.

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ABSTRACT

Fish derived bio-oils have similar properties to petroleum-derived fuel oils and therefore the potential to be an alternative energy source. The quality of bio-oil as a fuel is determined by the quality of the feedstock and processing conditions. Fish oil may have poor cold flow properties due to the heterogeneity of the lipid composition. Different oil extraction methods produce different levels of homogeneity with respect to lipids. In this study, oil was extracted from fish waste via three different processes; modified fishmeal (MFM), supercritical extraction using carbon dioxide (SC-CO_2), and soxhlet extraction. The quality of oil extracted (composition, thermal degradation, physicochemical, and flow properties) were compared. The SC-CO_2 extracted 91% and the MFM extracted 71% of the total oil contained in the fish waste. The SC-CO_2 oil is more than 86 wt% triglycerides, representing a more homogeneous oil than the MFM at 70 wt% and soxhlet at 66 wt%. The free fatty acid (FFA) of SC-CO_2 oil is lower than MFM and soxhlet oil, making it a better feedstock for biodiesel production. Polar lipids were most abundant in the soxhlet oil at 22.98 wt%, followed by the MFM oil at 18.35 wt% and SC-CO_2 oil at 7.39 wt%. The MFM oil exhibited a shear-thinning non-Newtonian behavior, while the SC-CO_2 oil was Newtonian. Overall, the oil from SC-CO_2 showed better fuel properties, particularly as a blend and/or replacement for heating oil, than the MFM and soxhlet oil and the process has the potential for a lower environmental footprint.

1. Introduction

Fish processing operations generate considerable quantities of edible and inedible by-products. Approximately 45 wt% of the total catch of fish is discarded as processing byproduct including heads, frames, trimmings, fins, skin and viscera (gut, liver, etc...) [1]. Fish oil recovered from fish residue varies considerably (between a mass fraction of 1.4% and 40.1%) depending on the species, tissue [2] and season. There is an increasing interest in obtaining edible fish oil from fish by-products in order to satisfy the demand of omega-3 enriched products. However, waste fish oils can have a low-value application (fuel oil/biodiesel) when the content of omega 3 fatty acids (EPA and/or DHA) or when the yield after the refining process are low [3]. Various studies have investigated waste fish oil as fuel for conventional combustors or diesel engines [4–7]. Fish oils have similar properties to petroleum-derived fuel oils such as calorific/heating value and combustion efficiency [5,8,9,4]. When compared to petroleum based fuels, biofuels have the advantage of lower toxicity, higher biodegradation rates (reducing impact in soil and water if spilled), no sulfur, and a higher flash point [5,8,10,11]. The quality of bio-oil as a fuel is determined by the quality of the feedstock and the processing conditions, which need to be carefully managed to obtain a high quality fuel [8,12]. Atabani et al. [13] showed biodiesel quality is a function of feedstock fatty acid composition, production, and refining method(s). Studies have demonstrated crude fish oil has poor cold flow properties such as lower lubricity and viscosity, and

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Nomenclature

ALC	alcohol(s)
ASTM	American Society for Testing and Materials
AMPL	acetone mobile polar lipid(s)
ANOVA	analysis of variance
AOCS	American Oil Chemists' Society
CASD	Centre for Aquaculture and Seafood Development
DAG	diacylglycerol(s)
DHA	docosahexaenoic acid(s)
DSC	differential scanning calorimeter
EE	ethyl ester(s)
EPA	eicosapentaenoic acid(s)
GC-FID	gas chromatography with flame ionization detection
GE	glycerol ether(s)
EK	ethyl ketone(s)
FAME	fatty acid methyl ester(s)
FFA	free fatty acid(s)
HC	hydrocarbon(s)
HHV	high heating value
HPLC	high performance liquid chromatography
ID	internal diameter
ME	methyl esters(s)
MFM	modified fishmeal
MK	methyl ketone(s)
MUFA	monounsaturated fatty acid(s)
MUN	memorial University of Newfoundland
PL	phospholipid(s)
PUFA	polyunsaturated fatty acid(s)
SC-CO_2	supercritical carbon dioxide
SFA	saturated fatty acid(s)
SFE	supercritical fluid extraction
SE	steryl ester(s)
ST	sterol(s)
TAG	triacylglycerol(s)
TGA	thermo-gravimetric analysis
TLC-FID	thin-layer chromatography with flame ionization detection

higher acidity compared to conventional diesel fuel [11]. This is because unrefined fish oil contains impurities such as free fatty acids (FFA), primary oxidation products, minerals, pigments, moisture, and phospholipids [14]. High FFA and/or phospholipid levels reduce fish oil fuel quality and additional refining processes are required such as neutralization and degumming. Phospholipids polymerize due to heat and form deposits that clog injectors, valves, build up on the combustion chamber walls and cylinder surfaces in engines [12,15]. Sediments may clog fuel filters and pumps [12,16]. As a result of poor storage conditions of feedstock, the hydrolysis of triglycerides in the presence of water leads to high FFA and results in low oil stability during storage [17] and corrosion during use [12,17]. Water in fuel oil decreases the heating value, impedes ignition and slows down flame propagation [12].

The presence and/or quantity of impurities are highly dependent on the fish oil extraction method [14]. Fish oil (edible and non-edible) can be recovered through several methods. The wet reduction process is one of most common process employed in high volume fish oil production but may require subsequent refining steps in order to improve the fish oil quality [18]. Other conventional fish oil recovery processes use either high temperatures and/or flammable or toxic solvents, which could result in loss of functional properties and deterioration of oil quality [8,19–21]. Supercritical fluid extraction (SFE) has been proposed in the extraction of high quality compounds from natural sources [22] including oil recovery from seeds/biomass, whole fish and/or fish by-products [23]. SC-CO_2 for oil recovery is an attractive option as it is a non-toxic, non-flammable, inexpensive and clean solvent [8,21–24].

The objective of this study is to investigate the quality of oil extracted from fish waste using SC-CO_2 process and compare to conventional processes. Salmon oil extracted from fish processing waste via three different methods; SC-CO_2, soxhlet, and modified fishmeal (MFM) was compared. Chemical composition, rheological or flow properties and thermal stability were compared to determine their feasibility as a fuel oil.

2. Materials and methods

The feedstock is a by-product of the fish industry; specifically the offcuts (offal) from farmed salmon (*Salmo salar Linnaeus*), from Cooke aquaculture provided by the Centre for Aquaculture and Seafood Development (CASD). The offal consisted of salmon heads, trimmings, and frames, discarded during peeling, cutting, and evisceration processes in the fish plant. The by-product collected 'as is' was frozen at −40 °C. The sample was crushed using a Hobart grinder to 5–10 mm equivalent diameter for freeze drying. The crushed sample was freeze dried at 0.133 bar vacuum and −47 °C for 24 h. The dried samples were blended using a Ninja professional blender (NJ-600 series 1000 W) to produce fine particles with average particle size of 0.1–0.68 mm. The average composition of the main components was approximately 29 wt% oil, 60 wt% water, and 11 wt% protein. Supercritical grade carbon dioxide (4.8–99.99%) from Praxair Co. was used. The obtained grounded sample contained approximately 7–10 wt% moisture content, 42–53 wt% fish oil, and 20–24 wt% protein. The total fraction of oil was determined by soxhlet extraction using hexane.

2.1. Oil recovery methods

The experimental setup for the SFE process is shown in Fig. 1 and consisted of Teledyne Isco Syringe pump D-series (model 260D) fitted with a cooling jacket to cool the CO_2 and a reservoir to store liquid CO_2. In each experimental run, 10 g of sample (dry basis) was loaded into a 13.6 mL extraction vessel, and connected to the SFE fluid delivery system. The extraction vessel and delivery tubes were wrapped with heating tape (Omega Engineering, Inc., USA; model HTWC101-010) to keep the system at the specified temperature. The extractions were performed between 40 and 80 °C and pressures from 15 to 35 MPa. The liquid CO_2 was

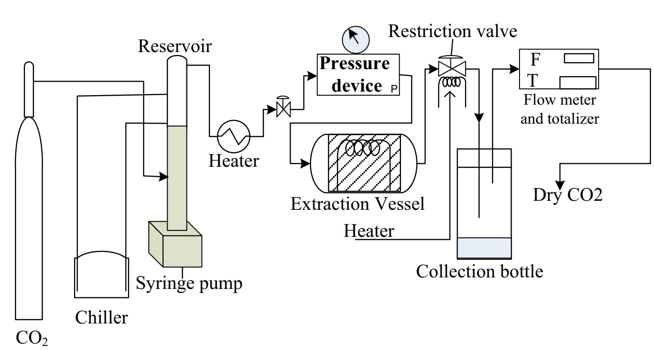

Fig. 1. Schematic diagram of experimental apparatus (supercritical CO_2 experimental setup).

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