



## Production of fuel from the catalytic cracking of pyrolyzed poultry DAF skimmings

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### ABSTRACT

A two-step thermochemical process, pyrolysis followed by catalytic cracking, was used to produce liquid fuels from poultry dissolved air flotation (DAF) skimmings, a waste material generated during poultry processing. Raw DAF-derived solids were dried and subjected to pyrolysis at 400, 500, 600 or 700 °C to thermally crack the material into three physical phases; a gas, solid, and liquid. The liquid phase, DAF bio-oil, was further processed in an attempt to produce a liquid fuel capable of powering a diesel engine. After catalytic processing and collection, the DAF bio-oil exhibited a higher heating value (HHV) of 36 MJ kg<sup>-1</sup>, which is less than the reported HHV of diesel (45.7 MJ kg<sup>-1</sup>), similar to biodiesel (36–40 MJ kg<sup>-1</sup>), but much higher than the HHV of bio-oil produced from the bioconversion of woody biomass (20 MJ kg<sup>-1</sup>). DAF bio-oil analysis generated measurements of HHV (MJ kg<sup>-1</sup>), cloud point (°C), viscosity (mm<sup>2</sup> s<sup>-1</sup> at 40 °C), and water content (%) revealed values of 36, 61.7, 37.8, and 4.72, respectively. After catalytic cracking, HHV increased to 40.2 MJ kg<sup>-1</sup>, cloud point decreased to -2.7 °C, viscosity decreased to 1.6 mm<sup>2</sup> s<sup>-1</sup>, and water content decreased to 1.9% making it comparable to conventional fuels. The upgraded DAF bio-oil could be utilized as a fuel for direct combustion in industrial boilers for steam generating, blended with petroleum fuels as an additive, or used directly as diesel transportation fuel.

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### 1. Introduction

Dissolved air flotation (DAF) is often used in the meat processing industry (poultry, swine, and bovine) to clarify wastewater by suspending and removing solids and oils. The byproduct of this process is a sludge with high moisture content (~70%) that consists primarily of fats and proteins. After the removal of organic material using DAF, wastewater can then be treated in conventional wastewater treatment systems. As an alternative, Sena et al. [1] showed that DAF processing followed by an advanced oxidation process could effectively generate an effluent with organic loads acceptable for discharge. However, the issue of what to do with DAF solid waste still remains. Much of the DAF waste is land-filled, land-applied as fertilizer or rendered for animal feed. All of these disposal methods present their own problems such as transportation and materials handling costs. In addition, high water content in DAF also poses a problem in rendering applications where additional fees for dewatering can be incurred. According to Render Magazine's 2006 Market Report, 4.3 mil tonnes of fat and grease were generated in the U.S. from the animal slaughter industry in 2006 [2]. The USDA publication, "Poultry – Production and Value

2008 Summary" [3], states that 8.9 bil broiler birds were produced in the U.S. in 2008. Based on an estimate of 34 g of DAF skimmings generated per bird [4], 303,000 tonnes of wet DAF was generated in 2008 from broiler production. As an alternative to disposal or rendering, this material could be converted into a liquid transportation fuel to help eliminate any disposal problems and would also serve as a value-added, marketable product derived from a waste stream.

Thermochemical approaches are often used to generate value-added products including liquid and gaseous fuels and activated carbons from a wide range of waste materials including fats and grease [5–8], wood [9–11], seed/nut waste [12–15], and agricultural residues [16,17]. Pyrolysis and catalytic cracking are two commonly utilized thermochemical conversion techniques. Each process generates products in three physical phases; a solid, liquid and gas. The solid phase remaining after pyrolysis contains most of the minerals, or ash, that if left in the material could pose problems in fuel applications. The removal of ash is particularly important in DAF upgrading due to relatively high levels (2%) that are present as a result of the use of polymers of acrylamide and ferric chloride which are used as flocculating agents [18]. The liquid phase evolved during pyrolysis and catalytic cracking can, when condensed, be used as a liquid fuel. Also evolved during thermal process, permanent gases may include CO, CO<sub>2</sub>, H<sub>2</sub>, and CH<sub>4</sub> along with many others including C<sub>2</sub>–C<sub>6</sub> gases in small concentrations.

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Adebanjo et al. [5] explored animal fat (lard) pyrolysis for which the oil produced exhibited a very similar cetane number (46) and higher heating value ( $40 \text{ MJ kg}^{-1}$ ) to those specified by ASTM D975, “Standard specification for diesel fuel oil.” Smith et al. [18] showed that pyrolysis of poultry processing DAF followed by solvent extraction could be used to improve the quality of DAF such that it resembles diesel. Lima et al. [6] produced diesel-like fuels from pyrolysis of vegetable oils. Many studies have used fixed-bed catalytic upgrading to produce fuels from plant-derived oils [7,8]. In Twaiq and Mohamed [7], a mesoporous acid catalyst was used to crack palm oil achieving an 80–90% yield of liquid hydrocarbons. Additionally, several studies have used zeolites to upgrade vegetable oils to liquid fuels via fluid catalytic cracking [9,19]. The prospect of producing liquid fuels from waste fats and oils has prompted commercial interest, as well. For example, Tyson Foods and ConocoPhillips placed a target of producing 175 million gallons of diesel from animal fats using conventional hydrotreatment processes in existing refineries in 2008. Using hydrotreatment, Conoco states that it is able to produce high-quality liquid fuels from fats. However, hydrotreatment technology cannot be scaled down to distributed small units because of the difficulties to produce and handle hydrogen in small systems [20].

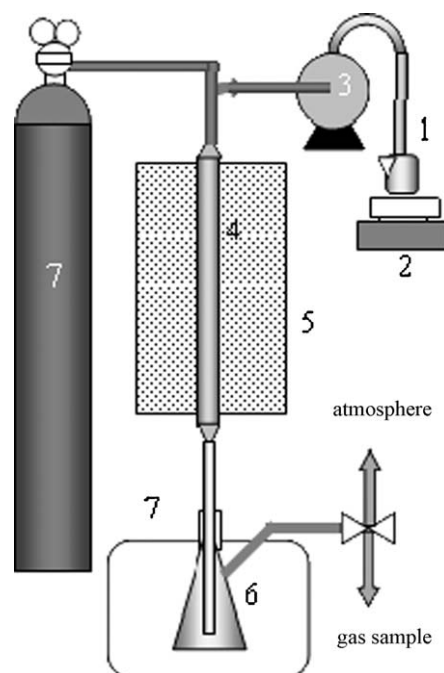
The overall goal of this project is to develop a thermochemical technology to convert dissolved air flotation (DAF) skimmings from poultry processing into a fuel using pyrolysis followed by catalytic cracking to produce renewable diesel and gasoline. Very little research has been devoted to the thermochemical transformation of DAF, and none found has attempted to generate “green” liquid fuels from the material. The main advantage of thermochemical conversion over widely used chemical conversion (transesterification) to produce biodiesel is that reaction time for thermochemical conversion is much shorter (seconds versus hours) such that a continuous flow system can be designed and integrated into poultry processing operations. In addition, the size and structure of resulting molecules can be better controlled in a thermochemical process to produce a bio-oil with desirable physical properties. Furthermore, catalytic cracking does not produce a liquid waste such as glycerol that is generated during transesterification.

## 2. Materials and methods

### 2.1. Pyrolysis of poultry DAF skimmings

Pyrolysis of raw DAF was performed in previous research, and detailed results are given elsewhere [18]. A brief description of the process will be described here. Using a batch reactor system, pyrolysis was performed at various temperatures with yields of solids, liquids, and gases determined by weighing the empty reactor vessel before the DAF was added so that both the weight of the sample used and the weight of char produced could be measured. The furnace was designed with two ports so that inlet and outlet lines could be connected to the reactor body for carrier gas and exhaust. A thermocouple was inserted into the reactor vessel so that the internal temperature of the sample could be measured during pyrolysis.

Pyrolysis was conducted at four different final internal temperatures ranging from 400 to 700 °C. The vapors were routed through a set of four condensers arranged with the first two in parallel and the subsequent two in series. The condensers were weighed before and after pyrolysis to determine the weight of bio-oil generated. The yield of the oil was then calculated using the weight of the oil produced relative to the initial weight of the DAF sample. The non-condensable gases that left the condensers were vented to the atmosphere. Liquid samples generated from the highest-yielding pyrolysis temperature runs were used in all subsequent catalytic upgrading steps. Thus, the control DAF sample, henceforth DAF BO, consists of raw DAF that has been pyrolyzed at 600 °C.



**Fig. 1.** Reactor setup showing (1) DAF BO vessel, (2) hot plate, (3) peristaltic pump, (4) stainless steel reactor, (5) tube furnace, (6) collection flask, (7) ice bath, and (8) compressed  $\text{N}_2$  tank.

### 2.2. Catalytic cracking

The catalytic upgrading experiment consisted of 6 treatments (performed in triplicate or 18 runs) in which three reaction temperatures (400, 450, and 500 °C) and two catalysts (H-ZSM-5 and FCC) were assessed. Cracking generated a solid, liquid and gas.

The main components of the upgrading system consisted of a 450 mm length, 23.8 mm i.d. reactor, a peristaltic pump, and an ice bath condensing system. The system, shown in Fig. 1, was packed with a 20–30 g fixed bed of catalyst, either pure zeolite (H-ZSM-5) or commercially available fluid catalytic cracking (FCC) variety. The H-ZSM-5 catalyst was produced by calcining  $\text{NH}_4\text{-ZSM-5}$  (Zeolyst International, CBV 5524 G) at 550 °C for 4 h to produce the hydrogen form, H-ZSM-5, resulting in stronger acid pore sites. The calcining process reduced the measured pH from 4.98 to 3.06. The catalyst has published values of  $425 \text{ m}^2 \text{ g}^{-1}$ , 0.46 mm, and 50 for surface area, particle size and  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio, respectively. The  $\text{NH}_4\text{-ZSM-5}$  catalyst was received from the manufacturer as a fine powder. In order to avoid clogging in the reactor, the catalyst was granulated by mixing with water, drying, crumbling, and sieving to the desired size, ~1–2 mm. The FCC catalyst was supplied by Grace Chemical – composition is proprietary. FCC catalyst was also supplied as a powder. Granulation was achieved in the same manner as H-ZSM-5.

Bio-oil, generated via pyrolysis of the DAF, was cracked using a reactor and process similar to that prescribed by ASTM D5154, “Standard test method for determining activity and selectivity of fluid catalytic cracking (FCC) catalysts by microactivity testing.” As advised, preheated oil, DAF bio-oil (DAF BO) in this case, was pumped into the reactor where it was vaporized and then passed over the catalyst bed maintained at 400, 450, or 500 °C. For H-ZSM-5 and FCC catalyst packing, 20 and 30 g of catalyst were used, respectively. Initially, a 20 g fixed bed was attempted using the FCC catalyst, but the higher density of the FCC catalyst resulted in shorter bed height relative to H-ZSM-5 and thus, shorter residence times for the bio-oil vapor. The product from the 20 g catalyst loading runs exhibited poor cold flow properties and no water formation indicating that very little cracking had been achieved. Thus,

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