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Title: Technoeconomic Analysis of Jet Fuel Production from Hydrolysis, Decarboxylation, and Reforming of Camelina Oil

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Abstract:

The commercial production of jet fuel from camelina oil via hydrolysis, decarboxylation, and reforming was simulated. The refinery was modeled as being close to the farms for reduced camelina transport cost. A refinery with annual nameplate capacity of 76,000 cubic meters hydrocarbons was modeled. Assuming average camelina production conditions and oil extraction modeling from the literature, the cost of oil was $0.31 \text{ \$ kg}^{-1}$. To accommodate one harvest per year, a refinery with 1 year oil storage capacity was designed, with the total refinery costing 283 million dollars in 2014 USD. Assuming co-products are sold at predicted values, the jet fuel break-even selling price was $0.80 \text{ \$ kg}^{-1}$. The model presents baseline technoeconomic data that can be used for more comprehensive financial and risk modeling of camelina jet fuel production. Decarboxylation was compared to the commercially proven hydrotreating process. The model illustrated the importance of refinery location relative to farms and hydrogen production site.

Technoeconomic Analysis of Jet Fuel Production from Hydrolysis, Decarboxylation, and Reforming of Camelina Oil

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1. Introduction

1.1. General Motivation

The development of biofuels can address concerns of sustainability, petroleum demand, and the environment. The U.S. Department of Energy (DOE) forecasts worldwide petroleum use will increase from 14 million cubic meters per day in 2010 to 18 million cubic meters per day in 2040 [1]. Though the U.S. is experiencing a crude oil boom, its future is uncertain. The DOE projects continued crude oil growth until 2036 under its High Oil and Gas Resource scenario, but under its Reference and Low Oil and Gas Resource scenarios, production will begin to decline by approximately 2021 and 2017, respectively [2]. Moreover, since the Energy Independence and Security Act of 2007, the U.S. has promoted the development of biofuels to reduce greenhouse gas emissions [3].

1.2. Commercialized Biofuel Processes

Ethanol and FAME (fatty acid methyl ester) biodiesel are biofuel replacements for gasoline and diesel, respectively. Several technologies for bio-jet fuel have met ASTM standards, including Fischer-Tropsch Hydroprocessed Synthesized Paraffinic Kerosene (FTH-SPK), Hydroprocessed Esters and Fatty Acids Synthesized Paraffinic Kerosene (HEFA-SPK), and fermented sugars hydroprocessed Synthesized Iso-Paraffins (SIP) [4]. HEFA-SPK utilizes triglyceride feedstocks such as plant oils and animal fats, and removes the oxygen via hydrogen, releasing water. The products are hydrocarbon-only fuels [5-6]. HEFA-SPK refineries of 116 dam³ per year and 378 dam³ per year were modeled using soybean oil as feedstock [7]. The refinery requires a large amount of hydrogen for oxygen removal.

Several companies have commercialized refineries utilizing the HEFA-SPK technology. Neste Oil has two refineries of annual nameplate capacity 190 Gg renewable diesel (approximately 238 dam³) in Finland, and two 800 Gg renewable diesel (approximately 1,000 dam³), one each in Singapore and the Netherlands [8]. The two Finland HEFA-SPK refineries are co-located with a petroleum refinery in the port of Porvoo [9]. The Singapore HEFA-SPK refinery is co-located with a large industrial zone at the coast [10]. The Netherlands HEFA-SPK refinery is co-located with other chemical plants in the port of Rotterdam [11]. The refineries have the capability to produce jet fuel [12]. In 2012 and 2013, the Neste Oil HEFA-SPK refineries used 64.5% and 47.4% crude palm oil respectively, 35.1% and 52.6% waste and residues (waste animal fat, waste fish fat, vegetable oil fatty acid distillates) respectively, and 0.3% and 0.0% other vegetable oils (rapeseed, soybean, camelina) respectively [13]. Renewable Energy Group (REG) has a HEFA-SPK refinery of annual nameplate capacity 284 dam³ fuel in Geismar, Louisiana [14]. The refinery has the capability to produce jet fuel. Diamond Green Diesel has a HEFA-SPK refinery of annual nameplate capacity over 568 dam³ diesel fuel in Norco, Louisiana near the Valero St. Charles petroleum refinery [15]. In summary, HEFA-SPK refineries have been commercialized, typically for the production of diesel but with jet fuel capability as well, and close to coasts and petroleum refineries.

An alternative conversion process from triglycerides to hydrocarbons is decarboxylation of the fatty acids [16]. A decarboxylation process has been selected for analysis, with data derived from a patent and additional studies [17-20]. Turner and Roberts [21] modeled the energy balance for the hydrolysis, decarboxylation, and hydrocarbon reforming steps, with a different

decarboxylation gas clean-up process than reported here, and found the process to be 89.6% energy-efficient.

1.3. Camelina

Camelina is in the Brassicaceae, or mustard, family and has been identified as an energy crop because of low input requirements, fast growing rate, good stress tolerance, high yield potential, and a sustainable life cycle [22-25]. Camelina is typically considered for production in the US. northwest. In 2007, 91 km² camelina were planted in Montana, though the value declined to 8 km² by 2012 [26]. Another source indicates that in 2009, 80 km² of camelina were planted in the U.S. [27]. Due to its short growing season, camelina could be rotated with wheat over a two year cycle. It is projected that from 2012 to 2024, annual U.S. wheat acreage will be 220,000 km² [28]. If camelina acreage rose to the level of wheat acreage, then given the calculations described in this paper, 15 hm³ fuel could be produced. Another way to quickly evaluate camelina potential is observing land use. For one example, in 2012 Montana had 242,000 km² “land in farms” (defined as agricultural land used for crops, pasture, or grazing, and including woodland and wasteland not actually under cultivation or used for pasture or grazing [29]) and of that, 28.5% was “total cropland,” 4.4% was “total woodland”, 65.8% was “permanent pasture and rangeland other than cropland and woodland pastured”, and 1.4% was “farmsteads, buildings, livestock facilities, ponds, roads, and wasteland” [30]. While this paper will not explore specific scenarios on land use, clearly, there is potential for camelina as a biofuel feedstock, without infringing on food production, by planting camelina in crop rotations and/or on marginal unused farmland. The crop has been evaluated as a feedstock for on-farm oil production and consumption [31].

Camelina has also been modeled as feed for diesel refineries using the HEFA-SPK technology [32].

1.4. Purpose

The purpose of this analysis is to provide knowledge on commercial jet fuel production from camelina. A technoeconomic model for the production of jet fuel from camelina oil via the decarboxylation technology was developed. This is not a comprehensive financial model, so some financial assumptions and determinants such as income tax, amortization, rates of return, and net present value are neglected. Rather, the data is presented simply without many embedded financial assumptions, so future financial modeling and risk management can be more clearly incorporated by the community.

Since the purpose of this paper is camelina jet fuel, the supply chain is very broad, including applications in agriculture, chemical refining, and associated logistics in both sectors. There are limitless variations that could be explored. It is important to characterize the interests and limits of this paper.

The selection of jet fuel as the primary product studied for this paper is because there is no widely available renewable alternative similar to ethanol and biodiesel used as gasoline and diesel replacements, respectively. However, there is unique demand for jet fuel. The United States Department of Defense Directive 4140.43 mandated JP-8, military jet fuel, as the universal military fuel [33]. Also, while military jet fuel demand is expected to remain steady

through 2035, the demand for commercial jet fuel is expected to increase by as much as 25% by 2035 [34].

Our baseline assessment is modeling a camelina oil decarboxylation refinery of annual nameplate capacity 76 dam³ hydrocarbon fuels, defined as the volume of fuel produced from the decarboxylation reactor. This is considerably smaller than the existing HEFA-SPK refineries. However, those refineries were not designed for a dedicated energy feedstock. Other technologies with refineries designed with dedicated energy feedstocks have been developed. Such refineries are close in size to the baseline assessed here. For example, the DuPont cellulosic ethanol refinery in Nevada, Iowa has a nameplate capacity of 113 dam³ ethanol and utilizes only corn stover, collected from a 48-km radius [35]. The Abengoa Bioenergy cellulosic ethanol refinery in Hugoton, Kansas has a nameplate capacity of 94 dam³ ethanol and utilizes corn stover, wheat straw, and grain sorghum residue collected from a 80-km radius [36].

A refinery with a dedicated feedstock, similar to the development of cellulosic ethanol refineries utilizing corn stover, may necessitate contracts between farmers and the refinery. As such, the refinery would be inclined to use the dedicated feedstock. To reduce risk, the refinery may have a flexible platform for alternative feedstocks, which would necessitate expertise in feedstock handling and process optimization for each of the feedstocks. However, another option is large feedstock capacity for the dedicated feedstock. To maintain our primary purpose of exploring camelina jet fuel production, we therefore maintain large feedstock capacity at the refinery. We acknowledge there may be other commercial scenarios beyond the primary purpose of this paper.

While existing HEFA-SPK and biodiesel refineries may use multiple feedstocks, this paper explores the use of camelina oilseed crop as a dedicated energy feedstock. This is similar to the development of cellulosic ethanol refineries, which use dedicated energy feedstocks. By aligning feedstock producers with the refiner, there is potential for favorable contracts. Similar to the development of cellulosic feedstocks with cellulosic conversion processes, this paper explores the potential for development of energy oilseed crops aligned with conversion processes. In this paper, expected average yields of camelina with advances in camelina crop production management are discussed. Under the stated yields and at the baseline refinery size, the land required would be around 295 km². As will be discussed in this paper, Montana camelina production has reached up to around 30% of that requirement in recent years. While much work in biology and agriculture is needed before camelina is produced at the scales sufficient for the refineries modeled in this paper, it is clear there is interest in camelina. This is but one work which illustrates camelina jet fuel from a demand view, but much work is still needed especially from a supply view.

Nevertheless, since the primary purpose is to investigate camelina jet fuel production, other alternatives besides the baseline are explored for comparison. For one, the decarboxylation technology is compared to the HEFA-SPK technology, at different locations and refinery sizes. Our hypothesis prior to the modeling effort is that because the decarboxylation technology removes oxygen catalytically rather than using hydrogen, it will have more favorable economics when the refinery is close to the camelina source. This is because agricultural production and hydrogen production are not typically co-located. Pearlson et al. [7] modeled on-site hydrogen production co-located with the HEFA-SPK refinery. Such a model of on-site hydrogen

production is not included here, but is discussed and is assessed indirectly by comparing hydrogen cost and delivery with location. Either hydrogen is produced and shipped, or natural gas is produced and shipped. While natural gas distribution is considerably easier than hydrogen distribution, there are still uncertainties. Limitless scenarios can be envisioned. This paper explores but a few of them.

2. Method for process design and economic model

2.1. Process model of hydrolysis, decarboxylation, and reforming

2.1.1. Hydrolysis

Figure 1 illustrates a schematic of the hydrolysis, decarboxylation, and reforming process simulated. The process was modeled in Aspen Plus® [37] to identify optimal conditions for separation processes. The refinery is fed camelina oil and water into the first reactor, the hydrolysis reactor. This process is common in the fatty acids industry, and a Colgate-Emery reactor is a typical design [38]. Wang et al. [19] reported 99.7% of theoretical yields for the hydrolysis step. Typical conditions are 250°C temperature and 5 MPa pressure. The outputs are product streams of free fatty acids (FFA) and glycerol. It is assumed that the conversion process is a one-step chemical reaction from one mole of water and one mole of triglyceride converting to one mole of FFA and one mole of glycerol. At steady-state operation, this assumption is justified. The FFA stream contains some residual MIU (moisture, insolubles, and unsaponifiables). The glycerol product stream also contains MIU, especially much of the excess water, and is commonly known as sweetwater. The sweetwater is purified in a two-step process: a flash distillation step and then a catalytic separation step. Optimal sweetwater flash conditions were found to be 125°C and atmospheric pressure. The FFA stream is purified and then sent to

the decarboxylation reactor. Optimal FFA flash conditions were found to be 200°C and atmospheric pressure.

2.1.2. Decarboxylation

The decarboxylation reaction requires hydrogen and nitrogen gases. In the reactor, the hydrogen saturates the double bonds on the FFA. Then, through a catalytic reaction, carbon dioxide is released from the FFA, yielding the n-alkane of one less carbon number than the FFA. Wang et al. [19] reported 90% of theoretical yields for the decarboxylation step. Ford et al. [39] reported decarboxylation results in 600-cm³ and 5,000-cm³ reactors. Thapaliya [40] reported turnover numbers of 10,000 (an indicator of catalyst lifetime) for catalytic decarboxylation in the 5,000-cm³ reactor (reactor scale-up and process optimization would enable investigation of maximizing turnover number). Typical decarboxylation conditions were 280°C and 2 MPa. A deoxygenation efficiency of 100% is assumed from engineering work in scaling the reactor to commercial size, with 95% of the deoxygenation contributed to decarboxylation reactions and 5% to decarbonylation reactions. The effluent gas product stream contains carbon dioxide (product of decarboxylation), carbon monoxide and water (products of decarbonylation), and excess hydrogen and nitrogen. The gas is cleaned in a two-step cooling process while maintaining the high-pressure environment. In the first step, the temperature is reduced to -20°C, condensing water. In the second step, the temperature is reduced to -80°C, condensing carbon monoxide and carbon dioxide. The condensed product stream containing the carbon oxides, referred to as dry ice, is, by volume, 94% CO₂, 3% CO, 2% N₂, and balance H₂ and H₂O. The gas product stream from the second step is the excess H₂ and N₂, which is recycled to the decarboxylation reactor.

2.1.3. Reforming

The n-alkanes are reformed, or isomerized and cracked, in the hydrocracking/isomerization reactor, in a set of reactions familiar in the petroleum, FTH-SPK, and HEFA-SPK processes [41]. Typical reforming conditions were 280°C and 6 MPa. The yields for optimizing to jet fuel were calculated based on the experiments of Abhari et al. [42]. They reported hydrotreating inedible tallow to n-alkanes via the HEFA-SPK process, and then hydrocracking and isomerizing the n-alkanes to a blend of fuels optimized for jet fuel. The liquid hydrocarbon mass yield from the hydrotreated/cracked tallow was 88.2%. Then, that product was isomerized/cracked and the liquid hydrocarbon mass yield was 91%. Then, that product was distilled and 88.9% met a broad jet fuel cut defined as C₈-C₁₆ hydrocarbons. Of the broad jet fuel cut, 77.2% were iso-alkanes with the balance n-alkanes. Hydrogen gas is added to saturate the alkenes produced from hydrocracking. The effluent gas stream is a mix of liquefied petroleum gas (LPG) and H₂, which is separated.

The blend of n- and iso-alkanes from the reforming reaction are separated in a fractional distillation column to product streams of diesel, jet, gasoline, and LPG. The cut heavier than C₁₆ is the diesel co-product. The cuts lighter than C₈ are separated into gasoline and LPG. Typical distillation conditions were approximately 200°C and atmospheric pressure.

2.2. Camelina oil profiling

Several studies have analyzed the fatty acid profile of camelina oil (e.g., [43-46]). Camelina oil is high in polyunsaturated fatty acids, especially linolenic acid. For the present modeling, typical

profiles were collected and then averaged to calculate the molecular formula of an average camelina oil molecule. A formula of $C_{58.11}H_{100.97}O_6$ was calculated. Therefore, it was assumed that each triglyceride contains three unsaturated fatty acid chains with 1.87 double bonds. This information is critical to calculate the hydrogen requirement.

2.3. Energy balance

The energy balance was calculated using Aspen Plus®. The non-random two liquid (NRTL) property method was used. Long-chain triglycerides were not in the components database, so properties were modeled using the Joback group contribution method [47]. Process energy is provided by a boiler fed the glycerol co-product from the sweetwater. A turbo generator is included in the system for combined cycle operations. Table 1 itemizes the energy inputs and glycerol energy output in the refinery. It is assumed that despite inefficiencies, the glycerol burner will supply sufficient energy for the refinery.

2.4. Capital costs

The Aspen operating model was then inputted to Aspen Icarus Process Evaluator® [48] for capital cost estimation. Icarus® has been used to model various biofuel refineries (e.g., [49-50]). Equipment modeled includes vessels, pumps, heat exchangers, valves, mixers, and splitters. Based on the specified equipment and the operating flow rates, pressures, temperatures, and stream components, Icarus® estimates the bulks (piping, instrumentation, paint, insulation, electrical, civil, steel, and nozzles) and construction. In addition to the packaged boiler units for burning glycerol and the steam-powered turbo generator, utilities include a derrick-supported flare stack, steam jet cooling system, and storage tank for waste. Some conditions selected for

Icarus® that helped guide the cost estimation are shown in Table 2. The costs are grouped by general purpose in Table 3. The capital costs have been converted from 2006 U.S. dollars, as modeled in Icarus®, to 2014 U.S. dollars using [51].

2.5. Economic parameters

2.5.1. Camelina oil cost

The cost of camelina oil production and the average camelina yield is taken from Miller et al. [32]. Camelina is planted, grown, and harvested with an average yield of 0.225 kg m^{-2} . Yield is a major risk for camelina or any crop. From 2007 to 2012, the average camelina yield in Montana was a low of 0.039 kg m^{-2} in 2012 and a high of 0.11 kg m^{-2} in 2010 [26]. Shonnard et al. assumed that through crop improvement research, future camelina yields could be 0.3 kg m^{-2} even while acknowledging recent yields were around 0.07 kg m^{-2} in 2007 [23]. Oil extraction utilizes solvent technology for maximum oil recovery, and the meal is sold for $0.26 \$ \text{ kg}^{-1}$. The minimum selling price for oil is therefore $0.31 \$ \text{ kg}^{-1}$. The oil extraction refinery has an annual capacity of 131 million kg oil, exceeding the requirements for the decarboxylation refinery with annual nameplate capacity 76 dam^3 hydrocarbons. The work of Miller et al. [32] suggests camelina is grown and harvested only once per year. Therefore, oil storage must be sufficient for 1 year. Then, the viability of long-term camelina oil storage must be considered. Several studies have cited the long-term viability of camelina seed and oil and similar vegetable seeds [52-54]. Oil storage is in flat bottom, flat roof storage tanks of stainless steel. Design specifications were based on industrial standards available in company brochures [55-56]. The oil is delivered at estimated costs [57] and insured.

2.5.2. Hydrogen gas cost

Linde Gas [58] estimates worldwide hydrogen production at 161 Mg hr⁻¹). Methods for transporting hydrogen include compressed gas delivery by truck, compressed gas delivery by rail, liquid hydrogen delivery by truck, liquid hydrogen delivery by rail, liquid hydrogen delivery by ship, metal hydride delivery by truck, metal hydride delivery by rail, and pipeline delivery. Hydrogen pipelines are limited. Lipman [59] reported that in 2006, pipeline mileage was mostly in: Texas (1363 km), Louisiana (467 km), Indiana (24 km), and California (21 km), with other states having 77 km. For a camelina refinery away from the petroleum refineries and pipelines, other options must be considered. Metal hydrides are not considered as the technology and commercialization appears to be still under development. Simbeck and Chang [60] estimate the cost of hydrogen gas production to be 1.30 \$ kg⁻¹, while liquid hydrogen costs 2.21 \$ kg⁻¹. Amos [61] calculated detailed costs for producing hydrogen based on type (gas or liquid), delivery method (truck, rail, ship, pipeline), amount (discrete values between 5 and 45,359 kg hr⁻¹), and distance (discrete values between 16 and 1,609 km).

For this study, the production costs from [60] and the delivery costs from [61] are selected as baseline parameters. It is assumed that the refinery is in a central U.S. location close to camelina production. According to West [62], U.S. hydrogen liquefaction plants are in California, Florida, Louisiana, Indiana, New York, and Alabama. It is thus assumed that hydrogen is produced and liquefied close to a coast, and then transported inland. The hydrogen is produced and liquefied at a cost of 2.21 \$ kg⁻¹ from the data of [60] and delivered by truck.

The explanation for liquid hydrogen delivery by truck is as follows. For liquid hydrogen delivery by truck, [61] calculated for a distance of 1,609 km, a production rate of 45 kg hr⁻¹ hydrogen has a delivery cost of 0.62 \$ kg⁻¹, and a production rate of 454 kg hr⁻¹ has a delivery cost of 0.50 \$ kg⁻¹. So assuming a linear relation, then the liquid hydrogen delivery cost by truck for long distance is calculated by Eq. 1,

$$\text{Delivery by truck of liquid H}_2 \text{ (\$ kg}^{-1}\text{)} = -.0003 * H_2 \text{ (kg hr}^{-1}\text{)} + 0.6332 \quad \text{Eq. 1}$$

For the requirement of 179 kg hr⁻¹ hydrogen in a 76 dam³ camelina jet fuel refinery utilizing decarboxylation technology, this truck delivery of liquid hydrogen cost is 0.58 \$ kg⁻¹. For the above scenario of long distance, the hydrogen gas delivery option by rail costs 2.39 \$ kg⁻¹ and the hydrogen gas delivery by truck option costs 9.87 \$ kg⁻¹. For the present study, hydrogen gas or liquid by rail will be excluded due to complex logistics, and hydrogen gas delivery by truck will be excluded due to extremely high delivery costs.

2.5.3. Returns

The prices for diesel, gasoline, and LPG are based on DOE projections. The annual projections [63] predict data to 2040. The prices from 2011 to 2040, all reported in 2012 U.S. dollars, were averaged. Since the process is not commercialized, there is risk whether the finished fuels would meet specifications. However, after decarboxylation, the process produces a stream of n-alkanes similar to that of the HEFA-SPK process, except the heaviest n-alkane has one less carbon than that of the n-alkanes from HEFA-SPK. Since the reforming steps of the HEFA-SPK process produce ASTM fuels, it is assumed that the commercialized decarboxylation process could

produce ASTM fuels. Dry ice is sold at 1.10 \$ kg⁻¹. This is significantly less than solid block dry ice retail prices such as 4.17 \$ kg⁻¹ [64]. The dry ice here is discounted because of its 3% CO by volume. The 24-hour Emergency Exposure Guidance Level is 0.005% CO by volume [65]. It is assumed that there is nearby offsite contract work for further processing, or special handling is available for delivery. The impact of dry ice selling price is further investigated later in this paper.

2.6. Results under baseline conditions

Table 4 lists the annual inputs, outputs, and unit costs and returns. It is assumed the lifetime operating load is 92%, or 1 month of shutdown per year for maintenance. Operators, supervisors, and maintenance are paid full-time regardless of shutdown.

2.7. Seed-to-oil processing

Long-term camelina oil storage is a risk without knowledge from further commercialization of camelina biofuels. Another possibility is co-location of seed-to-oil with oil-to-fuel processing, such that the seed is stored long-term rather than the oil. To pursue this option of risk management, a camelina seed processing model was designed. A model for the crushing procedure was developed using Aspen Icarus Process Evaluator®. Due to limited literature on crushing of camelina other than the work of Miller et al. [32], the model utilizes the literature data of the similar crops rapeseed and canola. In general, seed pressing is done either in small scale or industrial large scale [66]. In small scale pressing, cleaned oil seeds are mechanically pressed at 40°C. Suspended solids are removed by filtration or sedimentation. The press cake is left with oil content of over 10% by mass, which is used for fodder. Due to higher production

costs, small scale pressing production is not widely applied [66]. The industrial large scale process, rather, is preferred. For rapeseed, the seeds must be dried first if storage length is greater than 10 days. This reduces the water content from 15% to 9% by mass. Then the rape seeds are cleaned by temperature conditioning at 80°C and then pressed also at 80°C. This extracts 75% of the oil. The pressed raw oil is filtered and dehydrated. The press cake has 25% of the oil, and hexane solvent is added at 80°C.

Thus, the first step in camelina seed processing would be seed storage. Flat bottom, cone roof storage bins of carbon steel are modeled for capacity sufficient for 365 days. Design of seed storage containers was based on observation of industrial standards [55-56]. Seed drying is modeled in Icarus® with 4 400-kW centrifugal fans. After seed storage, a seed conditioning step is the first process in seed crushing. The seed is first conditioned at 100°C. Seed conditioning is important to improve solvent penetration, reduce the oil viscosity, prevent press smearing from coagulated proteins, and deactivate enzymes [66-67]. The next step is seed pressing. The selection of a screw press was based on the report of Mulder et al. [67], which said that is the standard press type for oilseeds of oil content greater than 25%. It is assumed that the camelina seed is 38.6% oil by mass. The sizing of the press is based on commercial literature. An oil press with capacity of 136,000 kg per 24 hours was identified [68]. The press was modeled in Icarus® using the brochure literature information. The hopper circulates the seed using a heated mixing arm powered by a 15-kW motor. The screw press is modeled as a gyratory primary crusher in Icarus®. The press is powered by two 93-kW motors. The base price for the press was inputted from the Cropland Biodiesel [68] company brochure to Icarus®, and then modeled in Icarus®, along with standard motors. This procedure allowed for the prediction of bulks, installation, and

operating requirements for a specific and critical piece of equipment not typically used in Icarus®. Two product streams are then produced, an oil stream and a cake stream. Cropland Biodiesel [68] reports 10-15% residual oil content in the meal. Though Cropland Biodiesel [68] lists several oilseed crops including camelina in its brochure, it does not specify if that oil content was measured for camelina. Nevertheless, this is lower than the 25% for rapeseed reported by Rutz and Janssen [66]. However, Mulder et al. [67] report 15-18% residual oil content in the meal for rapeseed. The cake stream is then inputted to a hexane solvent extraction reactor, where two output streams, called the miscella and grist, are produced after heating at 80°C. The use of a solvent extractor for camelina meal is reported in the company brochure of Natural Selection Farms [69]. Solvent extraction after pressing is commonly used for the industrial centralized large scale extraction of oil [66]. The miscella stream contains oil and hexane, and the hexane is separated in a vessel at 80°C and recycled. It is assumed that degumming of the oil is not needed due to the lack of catalyst in the hydrolysis step. The grist stream contains cake and hexane, and the hexane is separated at 80°C and recycled. It is assumed that the water content of the seed remains in the cake.

2.8. Comparison to HEFA-SPK camelina jet fuel refinery at different scales and locations

2.8.1 HEFA-SPK camelina jet fuel modeling

For comparison to decarboxylation, a HEFA-SPK camelina jet fuel refinery was modeled. Reaction steps and temperatures, pressures, and mass flow rates were available from Pearlson [70] whose work was derived from sources including Syntroleum, now REG in Geismar, Louisiana. For a refinery with annual nameplate capacity of 76 dam³ hydrocarbons, the annual hydrogen requirement is 2,311,445 kg under the conditions defined in Table 4. Table 5 shows the

capital cost items for the HEFA-SPK refinery. It should be noted that because HEFA-SPK is a commercially proven process, the settings in Icarus® were modified from those for decarboxylation. This was a significant reason that the Indirects cost, including contingency, is 56.6 M \$ for the HEFA-SPK refinery but 109 M \$ for the decarboxylation refinery.

2.8.2 Hydrolysis, decarboxylation, and reforming of camelina oil for refinery of nameplate annual hydrocarbon production capacity 378 dam³

To evaluate scale, the refinery size was multiplied by a factor of 5. All equipment was resized in Icarus®.

2.8.3. Transportation of camelina seed

A model for calculating transportation cost of seed was developed. For a refinery at the center of a circular area of land, the average haul distance R is derived from Overend [71] as

$$R = 0.7186 \tau (n \phi^{-1})^{0.5} (P M^{-1})^{0.5} \quad \text{Eq. 2}$$

Where τ is the tortuosity factor (ratio of actual distance travelled to line of sight distance), n is the number of pie-shaped slices for harvesting in a circular area with the refinery at the center of the circle, ϕ is the fraction of area planted for crop, P is the refinery scale in units of dry tons per day, and M is the biomass productivity in units of dry mass per hectare per year. The coefficient, 0.7186, is for a refinery operating 365 days per year; Overend [71] assumed 330 days per year and thus the derivations lead to a coefficient of 0.6833 in Equation 8 of that paper. For this study, we assume τ of 1.5 and include a seed loss rate from farm to refinery of 10%.

2.8.4. Results of comparing technologies at different scales and locations

To compare the decarboxylation and HEFA-SPK technologies directly, several scenarios were selected and key inputs were varied. One key input is the cost of hydrogen. Hydrogen cost varies due to production method and delivery method. Pearlson et al. [7] added onsite hydrogen production to the HEFA-SPK refinery and found that the option adds about 0.12 \$ kg⁻¹ for a refinery of 116 dam³ and about half that for a refinery of 378 dam³. Figure 2 compares several different scenarios as a function of hydrogen cost. All scenarios include a refinery with seed-to-oil processing co-located with oil-to-fuel processing, with fuel processing optimized for jet fuel production. For the scenarios inland, no location is exactly specified, but a location such as Montana is generally assumed. It is assumed that 30% of the land around the refinery is cropped for camelina once per year, so that the average camelina seed transport distance is 33 km. The refinery includes 1 year seed storage and 30 days hydrogen gas storage. For the scenarios coastal, no location is exactly specified, but a location such as Louisiana or California, close to petroleum refineries and where existing HEFA-SPK refineries are, is generally assumed. Furthermore, it is assumed that the average seed transport distance is 1815 km. The refinery includes 1 year seed storage and no hydrogen gas storage. Due to the location, hydrogen is accessible. For all refinery options, maintenance cost, operators, and supervisors are modified according to Icarus®.

Based on those few assumptions, wide results are observed. Figure 2 shows that the decarboxylation refineries inland would be most competitive, followed by the HEFA-SPK refineries inland. There is a saving of about 0.10 \$ kg⁻¹ when any refinery option is increased by

a size factor of 5. For coastal refineries, there is an increase of about 1.25 \$ kg⁻¹. The additional cost in seed transport has a larger impact than the saving in eliminating hydrogen gas storage.

As indicated earlier, the value of the dry ice from the decarboxylation refinery is uncertain. Figure 3 shows the variability in derived demand, or break-even, jet fuel selling price, as a function of the dry ice selling price. The entire decarboxylation gas clean-up process and also 30 days of dry ice storage is included in the capital cost of the decarboxylation refineries, regardless of whether the dry ice is sold for any value. For all eight scenarios shown, the hydrogen gas cost at the refinery gate is maintained constant at the baseline of 2.79 \$ kg⁻¹, though there would be some differences based on location. In general, if the baseline assumption throughout this paper of dry ice sold at 1.10 \$ kg⁻¹ has no validity and the dry ice has no value, then the jet fuel derived demand increases by about 0.25 \$ kg⁻¹ for any decarboxylation scenario.

3. Discussion

As shown in Table 4, the jet fuel break-even price is 0.80 \$ kg⁻¹. Pearlson et al. [7] assumed soybean oil at a cost of 0.75 \$ kg⁻¹ for their HEFA-SPK refineries. For the current study of the decarboxylation refinery, camelina oil at 0.31 \$ kg⁻¹ was used. If the feedstock cost was 0.75 \$ kg⁻¹, neglecting other differences such as hydrogen requirement difference for different fatty acid profiles, the jet fuel break-even price is 1.47 \$ kg⁻¹ in this decarboxylation study. The DOE [63] predicts the average jet fuel price in 2012 USD to be 1.00 \$ kg⁻¹ throughout 2011 to 2040. This suggests that decarboxylation processing of camelina oil has the potential to be competitive with petroleum, but the relative prices of camelina oil and petroleum feedstocks will be a critical determinant.

It is important to consider that decarboxylation has not been commercially proven. The results assume some scaling risk, such as the 18% contingency factor in the capital cost. Nevertheless, the model assumes that the decarboxylation catalyst will last for 11 months until replacement. For a different scenario, it can be assumed that the catalyst lifetime is only five months, so there are two one-month shutdowns each year. The lifetime operating load is thus reduced from 92% to 82%. The annual operating supplies and lab charges cost is doubled to account for the increase in decarboxylation catalyst, solvent, plus other unexpected replacement parts. The annual maintenance cost is also doubled to account for additional work required for catalyst replacement. In this scenario, the jet fuel break-even price increases from 0.80 \$ kg⁻¹ to 1.04 \$ kg⁻¹.

4. Conclusions

A technology incorporating hydrolysis, decarboxylation, and reforming of triglycerides to jet fuel was evaluated. Aspen Plus® was used for the energy balance and identification of optimal separation conditions. Icarus® was used for capital cost modeling. The refinery was modeled in a central U.S. location, close to the farms, so oilseed delivery cost was minimized. A module for hydrogen production and delivery from the coast to the refinery was included for high-fidelity simulation. If fed a low-value feedstock such as the energy oilseed crop camelina, the decarboxylation refinery can be competitive with petroleum prices.

The decarboxylation refinery was compared to the commercially proven HEFA-SPK refinery. The HEFA-SPK refineries are typically constructed at coastal locations for access to hydrogen,

but do not receive dedicated feedstocks. The results indicate that the benefits of considering decarboxylation are best realized for locating a refinery close to farms growing dedicated energy feedstocks. Dry ice co-product greatly benefits the economics of the decarboxylation refinery, but more work would be needed in improving dry ice product quality to ensure a marketable product.

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Figure captions

Figure 1: Schematic of the hydrolysis, decarboxylation, and isomerization/hydrocracking process per Roberts et al. [17].

Figure 2: Comparison of decarboxylation and HEFA-SPK camelina jet refineries under different scenarios. Each refinery includes camelina seed crushing and oil-to-fuel conversion. Economic parameters come from Tables 1-5 unless specified otherwise. For refineries described as “coastal” no hydrogen gas storage is included in the capital cost and the average seed transport distance is 1815 km. For refineries described as “inland” 30 d hydrogen gas storage is included in the capital cost and the average seed transport distance is 33 km. Project lifetime is 20 years.

682

683 Figure 3: Comparison of decarboxylation and HEFA-SPK camelina jet refineries under different
684 scenarios of dry ice selling price. Each refinery includes camelina seed crushing and oil-to-fuel
685 conversion. Economic parameters come from Tables 1-5 unless specified otherwise. For
686 refineries described as “coastal” no hydrogen gas storage is included in the capital cost and the
687 average seed transport distance is 1815 km. For refineries described as “inland” 30 d hydrogen
688 gas storage is included in the capital cost and the average seed transport distance is 33 km.
689 Project lifetime is 20 years.

Tables

Table 1: Energy requirements from the decarboxylation refinery.

Item	Energy (kW)
Pre-hydrolysis water heater	2,030
Pre-hydrolysis water pump	14
Camelina oil pump	15
Hydrolysis reactor	76
Sweetwater flash vessel	1,281
Fatty acid pump	6
Decarboxylation reactor	357
Decarboxylation water product condenser	161
Decarboxylation carbon oxides product condenser	154
n-Alkane pump	15
Isomerization/hydrocracking hydrogen compressor	70
Total requirement	4,179
Glycerol burner	-6,588

Table 2: Icarus modeling assumptions.

Process Assumptions	
Process Description	New & Unproven Process
Process Complexity	Typical
Process Control	Digital
Project Information	
Project Location	North America
Project Type	Grass roots / Clear field
Contingency %	18
Estimated Start of Basic Engineering	1 Jan 13
Soil Condition Around Site	Soft Clay
Equipment Specification	
Pressure Vessel Design Code	ASME
P and I Design Level	Full

Table 3: Capital costs for decarboxylation refinery, optimized for jet fuel, of 76 dam³ hydrocarbons annual nameplate capacity. Numbers may not add due to rounding.

Equipment	Notes	Total Direct Installed Cost including Equipment & Setting, Piping, Civil, Structural Steel, Instrumentation, Electrical,
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		Insulation, and Paint (2014 USD)
Camelina oil storage	For 1 yr	102 M
Hydrolysis	Hydrolysis reactor, fatty acid/water product separator, glycerol/water product separator, glycerol purifier, heat exchanger, heater, 2 mixers, 2 pumps, 3 valves	3.14 M
Decarboxylation gas storage	For 30 days	19.8 M
Decarboxylation	Decarboxylation reactor, water product condenser, carbon oxides product condenser, pump, valve, mixer	1.86 M
Dry ice storage	For 30 days	3.31 M
Reforming gas storage	For 30 days	25.5 M
Reforming	Isomerization/hydrocracking reactor, compressor, mixer, valve, pump	2.69 M
Distillation	Distiller, reboiler, condenser, gas separator, 2 valves	2.89 M
Fuel storage	Jet fuel, diesel, gasoline, and LPG for 30 days	8.77 M
Utilities	Glycerol burner, turbo generator, waste tank, flare, steam jet cooler	3.46 M
Indirects	Project area, engineering, taxes, contingency	109 M
Total		283 M

Table 4: Annual production and return costs, assuming 92% operating load and 30-yr project lifetime. 8765.81 hrs/yr. Numbers may not add due to rounding.

Operating Expense	Annual Consumption	Units	Unit Cost	Annual Expense (\$)	Notes
Camelina oil	66,424,560	kg	0.31 \$	20,591,614	Unit cost from [32]
Oil delivery	2,138,000,664	kg km	0.00020548 \$	439,323	Delivery

					distance of 32.1869 km with cost estimation from [57] of 0.00021 \$ kg ⁻¹ km ⁻¹
1-yr Oil storage insurance	20,591,614	%	2	411,832	
Hydrogen	1,441,851	kg	\$2.79	4,022,765	Liquid hydrogen production modeled from [60] and delivery by truck from coast to central US modeled from [61]
General & administrative	1	\$	8% of all other operating expenses	2,699,756	Icarus baseline factor
Operating supplies and lab charges	1	\$	1,120,000	1,120,000	Estimated from [18-20]
Overhead	1	\$	50% of Operators, Supervisors, and Maintenance	2,338,280	Icarus baseline factor
Maintenance	8,765.81	hour	402.50 \$	3,528,239	Icarus calculation
Operators	35,064	person-hour	24 \$	841,518	Icarus calculation
Supervisors	8,766	person-hour	35 \$	306,803	Icarus calculation
Nitrogen	237,997	kg	0.61 \$	145,178	
Water	15,880,640	kg	0.000088 \$	1,398	Unit cost from [7]
Capital (2014	1	\$	9,422,600	9,422,600	Converted

USD)					from 2006 USD in Icarus to 2014 USD using 1.18X Consumer Price Index from [51]
Interest on 70% Capital	1	\$	16,609,397	16,609,397	Converted from 2006 USD in Icarus to 2014 USD using 1.18X CPI
Production Total	1	\$	63,446,252	64,093,084	
Returns					
Dry Ice	9,788,568	kg	1.10 \$	10,767,425	94% purity
Diesel Fuel	4,055.456	m ³	1,070 \$	4,323.615	2011-2040 projected average of [63] in 2012 USD
Gasoline	3,407.923	m ³	900 \$	3,056.018	2011-2040 projected average of [63] in 2012 USD
LPG	4,723,387	kg	1.26 \$	5,951,468	2011-2040 projected propane average of [63] in 2012 USD
Jet Fuel – break-even	58,725.341	m ³	650 \$	38,353.340	

Table 5: Capital costs for HEFA-SPK refinery, optimized for jet fuel, of 76 dam³ hydrocarbons annual nameplate capacity.

Equipment	Notes	Total Direct Installed Cost including Equipment & Setting, Piping, Civil, Structural Steel, Instrumentation, Electrical, Insulation, and Paint (2014 USD)
Camelina oil storage	For 1 yr	87.1 M
Hydrotreating	Hydrotreating reactor, 2 compressors, 2 heat exchangers, mixer, 1 pump	5.71 M
Hydrotreating gas storage	For 30 days	119 M
Gas/liquids clean-up	Preflash wastewater/gas separator, hydrogen/carbon dioxide/liquids pressure swing adsorption, propane/wastewater flash separator, liquids/lights distillation	967 k
Reforming gas storage	For 30 days	40.7 M
Reforming	Isomerization/hydrocracking reactor, compressor, mixer, valve, pump	4.09 M
Distillation	Distiller, reboiler, condenser	2.78 M
Fuel storage	Jet fuel, diesel, gasoline, and LPG for 30 days	8.93 M
Utilities	Boiler, turbo generator, waste tank, flare, steam jet cooler	3.46 M
Indirects	Project area, engineering, taxes, contingency	56.6 M
Total		329 M

Figures