



# DOTTORATO DI RICERCA IN

# GESTIONE SOSTENIBILE DELLE RISORSE AGRARIE FORESTALI E ALIMENTARI

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COORDINATORE

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## ENVIRONMENTAL IMPACT OF BIOPRODUCTS DERIVED FROM NON-CONVENTIONAL OLEAGINOUS: FALSEFLAX (*Camelina* sativa), SAFFLOWER (*Carthamus tinctorius*), CRAMBE (*Crambe* abyssinica) AND FLAX (*Linum usitatissimum*)

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#### Abstract

The growing demand of raw materials for the bio-refineries and the increase in bio-products demand could be considered important opportunities for agriculture worldwide. Among the innovations, it is expected the introduction of new food and non-food crops resulting in an increase in biodiversity as well as an environmental impact reduction achieved by replacing conventional refinery products. Nowadays, industrial bio-refineries were identified as one potential solution that may help mitigate the threat of climate change and the seemingly boundless demand for energy, fuels, chemicals and materials. Vegetal oils extracted from non-food crops are good source for bio-jet fuel that has drawn, in recent years, attention from commercial ventures and airlines. The concept of sustainability is becoming increasingly important, not only in energy industry, likewise in paper industry and trout harvesting industry around the world. In order to improve its environmental performance, these industries have made important investments, not only in the production process itself, but also in the flue gases and liquid effluents treatment systems. Besides this concern regarding pollution prevention. one of the issues of most relevance in the context of sustainability is replacing wood pulp mills with non-wood ones and replacing fish meal with locally produced oil meals. In this regard, the present work analyzes the life cycle (LCA) in a cradle to grave vision of products and by-products from processing of seeds, crop residues and oil extraction residues, of Camelina, Safflower, Crambe and Flax cultivate in Bologna and Pisa along three years. The aim is to evaluate the environmental impact due to the production chain of bio-products with different functionalities.

In this dissertation, we evaluated the environmental impact of renewable jet fuel (Bio-jet fuel) derived from Camelina, Flax, Crambe and Safflower oils, whose were extracted by cold press process and then were processed into bio-jet fuel. The indicator chosen was the Global Warming Potential (GWP) referred to the functional unit (1 MJ of Bio-jet Fuel) and its associated by-products (meal for Camelina and Safflower and straw for Flax; additionally, there was no well-known

Crambe's by-products applications). Impacts of the farming and extraction phases were determined with agronomic and qualitative data obtained from three years surveys, as part of the SUSCACE project activities in Pisa and in Bologna. As source of secondary data, several publications were used regarding oil-to-jet process as well as by products processes. BioGrace and Ecoinvet data bases were consulted to obtain the emission factor used, while the impact assessment of mainstream from farming to oil extraction was performed according to IPCC recommendations and ISO guidelines to perform LCA, considering the transformation processes implemented for the exploitation of by-products obtained along the entire production chain including transportation.

Results of LCA were compared with those of equivalent conventional products (fossil jet fuel, eucalyptus wood and fish meal). Regarding the cultivation phase of Camelina, the impact related to the functional unit or to a hectare in Bologna was found to be on average higher than that in Pisa, as consequence of a greater diesel requirement, and considerable lower yield in Pisa. On the other hand, GWP associated to Flax, Crambe and Safflower were lower in Bologna regarding farming phase. However, it is relevant to show that N-requirements of Bologna were considerably lower than Pisa in all crops. Consequently, N2O emissions are lower in Bologna with significant repercussions on the impact of the final product and on each step along. Furthermore, in extraction phase the variability of environmental performance has been influenced by oil content (%), leading flax oil to be less harm oil in terms of GWP. Considering GWP of bio-jet fuel, Flax derived bio-jet fuel has demonstrated being the best performed in both sites, considering the worst case was the environmental performances of Camelina derived jet fuel in Bologna and Cartamo derived bio-jet fuel in Pisa, the tendency was the same using allocation or system expansion method in order to reduce and reassigning impacts.

To conclude, Flax crop in both sites has a great performance in terms of environment protection, and it was contrasted with conventional product and with similar bio-products. However, the best environmental results in Bologna were obtained in the system expansion of Cartamo bio-jet fuel followed by the Flax derived jet fuel, both have produced negative GWP representing a real reduction in emission due to use of biofuel in aircrafts. Contrastingly, the worst performance was obtained by Camelina derived jet fuel. The behavior in Pisa was different, in first place Flax derives jet fuel as the best performance followed by Camelina one and the worst performance was attributed to Cartamo bio-jet fuel. Regarding the end life scenario, the advantage of bio-products derives from their biodegradability that substantially reduces or eliminates the disposal processes and their lower toxicity when it is compared to fossil-based product.

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## CHAPTER 1

### 1. Introduction

## 1.1. Project and objective

Considering the study in context of *"PROGETTO SUSCACE, SCHEDA AGRICOLTURA PER BIOPRODOTTI (AXBB) VALUTAZIONE DI SOSTENIBILITÀ DELLE COLTURE SVILUPPATE*<sup>"</sup> project and related subprojects, it's been presented the objectives to achieved in this work.

The project proposes, for three years (surveys) 2013-2015, to experimentally implement the inclusion of these crop systems (Falseflax (*Camelina sativa*), Safflower (*Carthamus tinctorius*), Crambe (*Crambe abyssinica*) and Flax (*Linum usitatissimum*)) in two areas: Bologna (Pianura Padana) and Pisa (Pianura Pisana) characteristic of the Italian pedoclimatic conditions. Sustainability assessment system will be developed, using the Life Cycle Assessment methodology, taking account of the savings (substitution values) emissions, the carbon sequestered by the residue digging, the reduction of impacts due to the reduction of transport and the possibility of using waste and by-products to produce other materials or bioenergy. The use of several naturally occurring materials produced locally to manufacture different products is a second or third-generation biorefinery linked to the land that, due to the specific nature of agricultural production, cannot be relocated.

#### **1.2.** Problem setting

Vegetable-based products (Bio-based Bb) are increasingly demanded by consumers all around the world, and some of these, particularly produced with non-conventional crops and their residues, can now represent an opportunity for agriculture to have new bio-based products and feedstocks, and to include them in cereal rotations. Many high-quality crops have been identified, from which raw materials can be obtained that could improve or replace some of imported raw materials or feedstocks, mainly for the areas of natural cosmetics, animal and fish feeds, nutraceutics, biomolecules production, lubricants, and bio-building. The benefits would be to increase agricultural biodiversity and the Eco-compatibility of end products and residues, enabling crops and waste to be available for bioenergy production as well. However, environmental burden associated to these crops is not well known, at present it is very important to assess it in order to establish their environmental impacts and sustainability in tested zones.

#### 1.3. Dissertation objective

To assess the environmental performance of non-food crops Falseflax (Camelina sativa), Safflower (Carthamus tinctorius), Crambe (Crambe abyssinica) and Flax (Linum usitatissimum) into bioenergy production and alternative uses of by-products considering the Global Warming Potential as indicator of their performance and considering system expansion where it is possible.

#### 1.4. Project overall and partners

For years, in Europe, the policy adopted to address the social and economic development of Member States in a sustainable manner places environmental issues at the forefront. In this context, it was evident the willingness and commitment to define broad-ranging strategies that would favor the transition to new production paradigms and economic models characterized by more efficient use of resources, a significant reduction in gas emissions Climbers, an improvement in the quality of ecosystems and well-being.

To do this, a system approach is needed that takes due account of the numerous and heterogeneous components that compete, as well as the complex interactions that arise between them. Defining at a European and national level a clear and straightforward path to follow is therefore very difficult, but it becomes even more complicated when it comes to working in the concrete on the territory where technical, legal and even specific cultural crises of the different local ambitions arise. Finally, the products and by-products coming from the supply chains under the "*PROGETTO SUSCACE, SCHEDA AGRICOLTURA PER BIOPRODOTTI (AXBB) VALUTAZIONE DI SOSTENIBILITÀ DELLE COLTURE SVILUPPATE*", the AxBB sub-project, will be considered and identified according to the current legislation.

The data used in this work was taken from a three-year (2013–2015) survey carried out in the experimental farm fields of Pisa and Bologna within the subproject *"MATERIE PRIME AGRICOLE ITALIANE PER BIOPRODOTTI E BIOENERGIE*" (AxBB), project that involves a research team:

- University of Bologna (UNIBO),
- University of Florence (UNIFI),
- University of Pisa (UNIPI) and
- Consiglio per la ricerca in agricoltura e l'analisi dell'economia agraria (CREA).

## **CHAPTER 2**

#### 2. Literature review

#### 2.1. Green Chemistry

Green chemistry is a pro-active approach to pollution prevention and mitigation. It targets pollution mitigation at the design stage, before it even begins and until to the end of life of a product and good related to a chemo process. Whether chemists are taught to develop and innovate products, feedstocks, supplies and materials in a manner that do not use hazardous substances, then increasing waste, hazards, and cost should be avoided (P. Anastas & Eghbali, 2010; Warner, Cannon, & Dye, 2004). Green Chemistry is designing chemical products and processes that reduce or eliminate the use and/or the generation of hazardous substances. In other words, it is a more sophisticated way of doing chemistry, aiming at preventing pollution, ecotoxicological and human-health problems at the chemical design stage (Chan, 2011). Hence it is more of a 'chemistry FOR the environment', (i.e. a more environmentally friendly chemistry) than a 'chemistry OF the environment', (i.e. chemistry that explains nature and the impact of man on the nature).

The American Chemistry Society (ACS) in its webpage defines green chemistry as "Sustainable and green chemistry in very simple terms is just a different way of thinking about how chemistry and chemical engineering can be done. Over the years different principles have been proposed that can be used when thinking about the design, development and implementation of chemical products and processes. These principles enable scientists and engineers to protect and benefit the economy, people and the planet by finding creative and innovative ways to reduce waste, conserve energy, and discover replacements for hazardous substances".

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To precede with green chemistry properly, 12 principles were recommended by (P. Anastas & Eghbali, 2010; P. T. Anastas & Warner, 1998 and ACS):

- **Prevention.** It is better to prevent waste than to treat or clean up waste after it has been created.
- Atom Economy. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
- Less Hazardous Chemical Syntheses. Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
- **Designing Safer Chemicals**. Chemical products should be designed to affect their desired function while minimizing their toxicity.
- Safer Solvents and Auxiliaries. The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
- Design for Energy Efficiency. Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
- Use of Renewable Feedstocks. A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
- Reduce Derivatives. Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
- **Catalysis.** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
- **Design for Degradation.** Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
- Real-time analysis for Pollution Prevention. Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

 Inherently Safer Chemistry for Accident Prevention. Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

#### 2.1.1. Green chemistry framework in Europe

Directive 2008/98/EC of the European Parliament represent the most relevant Community legislation for Green chemistry in the European Union (EU). This Directive establishes a framework for the treatment of waste and residues within the Community members. The directive defines some basic concepts, such as waste, residue, recovery, and disposal, and sets out the essential requirements for waste management in green chemistry framework.

The article number 5 of Directive 2008/98/EC, specifically refers to by-products. The inspirational principle of the legislator is that an object or substance should be considered by-products only when certain conditions occur in the process.

#### Article 5 By-products

1. A substance or object, resulting from a production process, the primary aim of which is not the production of that item, may be regarded as not being waste referred to in point (1) of Article 3 but as being a by-product only if the following conditions are met: (a) further use of the substance or object is certain; (b) the substance or object can be used directly without any further processing other than normal industrial practice; (c) the substance or object is produced as an integral part of a production process; and (d) further use is lawful, i.e. the substance or object fulfils all relevant product, environmental and health protection requirements for the specific use and will not lead to overall adverse environmental or human health impacts.

2. Based on the conditions laid down in paragraph 1, measures may be adopted to determine the criteria to be met for specific substances or objects to be regarded as a by-product and not as waste referred to in point (1) of Article 3. Those measures, designed to amend non-essential elements of this Directive by supplementing it, shall be adopted in accordance with the regulatory procedure with scrutiny referred to in Article 39(2).

On 2<sup>th</sup> December 2015, the European Commission adopted a new package of measures on the circular economy to promote the transition of Europe to a circular economy that, in intentions, will increase global competitiveness, will support economic growth, and generate new employment and reduces the human impact in the environment. The legislation was created by the previous *Barroso Commission*, but the current Junker commission withdrew it immediately, as soon as it was established, and then pledged to reappear it in response to criticisms received on that occasion. The comparison between the two proposals demonstrates that the current proposal is less determined than the former in achieving the objectives.

The new group of legal measures, including some legislative proposals on waste, landfills, residues and packaging, represents a global action plan that sets a concrete mandate for the duration of this Commission. Proposals on waste, despite the reduction compared to the previous proposal, have a clear and ambitious long-term vision to increase recycling and reduce landfill, while proposing concrete measures to overcome the obstacles to improved management of waste.

The package conceives substantial changes to some directives in force for several years (Waste, Dumps, and Packaging), only communications concerning other (WEEE and end-of-life vehicles) and finally only a report on the Batteries and Accumulators Directive.

i) Framework Directive 2008/98 / EC amended by the new proposed Directive on 2 December 2015

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ii) Dumping Directive 31/1999 / EC amended by the new proposed Directive on December 2, 2015

iii) WEEE Directive 2012/19 / EU amended by the new proposed Directive on 2 December

iv) Vehicle Directive at end of life 2000/53 / EC as amended by the new Directive proposed on 2 December 2015

v) Packaging Directive 94/62 / EC as amended by the new proposed Directive on 2 December 2015

vi) Batteries and Accumulators Directive 2006/66 / EC as amended by the new proposed Directive on December 2, 2015.

#### 2.1.2. Biorefineries context

The transition to third-generation biofuels and bioproducts is driven by the need to integrate biomass-derived fuels (Diesel, Gasoline and Jet Fuel) more seamlessly into the existing petroleum based infrastructure (Fatih Demirbas, 2009; Miller & Kumar, 2013) and another petroleum based products such as: petroleum jelly, lubricants, plastics, hydraulic oil, and so on. On the other hand, ethanol, whether derived from corn or sugarcane in first-generation processes or biomass in second-generation facilities, has limited market access due its dissimilarity to conventional petroleum-derived fuels (Hughes, Gibbons, Moser, & Rich, 2013). However, alternatives like butanol can be more suitable in several regional contexts.

Several limitations including restrictions on: ratios in which ethanol can be blended with gasoline (usually 5-10%), lack of compatibility with diesel, gasoline or jet engines, inability to transport ethanol through existing pipeline network, and propensity to hydration (Valdes, 2011). While it is clear that biomass can provide a sustainable and renewable source of carbon to replace a significant portion of petroleum or mineral carbon resources currently used to generate fuel, power, electricity and chemicals (Stokes & R.D. Perlack, 2011), it is also obvious that technologies must be developed to convert biomass into direct replacements for petroleum products. This transition to third-generation biofuels will involve numerous sides, the ideal scenario likely being a multipurpose biorefinery that utilizes many inputs and produces an even greater number of products or feedstocks (D'Avino, Dainelli, Lazzeri, & Spugnoli, 2015; Pradhan, Shrestha, Van Gerpen, & Duffield, 2008).

First-generation biorefineries are based on direct utilization of classical forms of agricultural biomass (Agricultural and forestry products; Agricultural and forestry residues) as shown in figure1. As production levels have increased, along with human populations, concerns about competition with food have growth exponentially (Fatih Demirbas, 2009). Nevertheless, over the past 30 years these first-generation feedstocks have paved the way for production of biofuels via a more sustainable system without negative impacts on the environment or food supplies (Fatih Demirbas, 2009). Second-generation biorefineries are based on biomass feedstocks that are more widely available and that are not directly used as food, although some are used as livestock feed. Technologies are under development to efficiently convert biomass into ethanol as well as valuable co-products. These are leading the way to sustainably meeting energy needs while also supplying materials for chemical and manufacturing industries (Demirbas, 2009).

Biomass has the unique advantage among renewable energy sources that it can be easily stored until needed and provides a liquid transportation fuel alternative for the near term. However, cellulosic ethanol can displace only the 40% of a barrel of crude oil that is used to produce light-duty gasoline (A. Dávila, Rosenberg, & A. Cardona, 2016). Research, development, and demonstration on a range of technologies are needed to replace the remaining 60%, which is primarily converted to diesel and jet fuel. About 15% of our current crude oil consumption is used to produce solvents, plastics, cleaners, adhesives and so on. Thus, cost-efficient technologies are needed to produce biofuels that are suitable for use in cars, trucks, electricity generators and jet planes. These advanced biofuels can be sustainably produced from cellulosic, oil seeds, and algal feedstocks (Stokes & R.D. Perlack, 2011). Biomass conversion technologies are also needed to produce chemical intermediates and high-value chemicals that can be used in many sectors as: chemical, pharmaceutics, nutraceutics, food and feed and so on.

Figure 1. Organization of industrial production of first and second-generation biomass biorefineries (sugar cane example) taken from (Valdes, 2011).



Biorefining has been defined as the sustainable processing of biomass into a spectrum of marketable products and energy. The biorefinery of the future will conduct many types of processes, including those producing advanced biofuels, commodity chemicals, biodiesel, biomaterials, power, and other value-added co-products such as sweeteners and bio insecticides (Moncada, Tamayo, & Cardona, 2014; Snell, Singh, & Brumbley, 2015). Beside the tools provided by molecular biology, environmental analysis and chemical engineering, the types

of co-products, chemicals and biofuels that can be derived from biomass may be almost limitless.

Figure 2. Bio-refinery scheme. Biomasses, products, and resources those are admissible in.



Biorefineries combine the necessary technologies for fractionating and hydrolyzing biological raw materials (oils, biomass, cakes with conversion steps to produce and then recover intermediates and final products. The focus is on the precursor carbohydrates, lignin, oils, and proteins, and the combination of biotechnological and chemical conversion processes of the substances (de Jong & Jungmeier, 2015; Taylor, 2008). Most of these processes are being developed

individually, but have the potential to be more efficient and economical when combined in multi-process crossover regimens using by-products or waste materials from one process to produce advanced animal feeds, human nutritional supplements, high-value peptides, enzymes, or mid-step chemical needed in other processes (Naik, Goud, Rout, & Dalai, 2010; Pelletier, 2009), these concept are illustrated in figure 2. Use of existing infrastructure would significantly decrease the time required for economical large-scale production of second and third generation biofuels.

To achieve the requirement for safe and sustainable energy production, thirdgeneration biorefineries must be better integrated, more flexible, and operate with lower carbon and economic costs than second-generation facilities as recommended by ACS (R. A. Lee & Lavoie, 2013; Moncada et al., 2014). Technology is developing rapidly in these areas. One of the principal tasks is to identify the most promising bio-based products, in particular food, feed, valueadded materials, active compounds, and chemicals to be co-produced with energy to optimize overall process economics and minimize overall environmental impact (D'Avino et al., 2015; Nasopoulou & Zabetakis, 2012). According to (Hughes et al., 2013), challenges to achieve optimal production rates of advanced biofuels include: overcoming biomass recalcitrance, logistics of transportation of raw feedstock and finished products, providing fair prices for crops or agricultural residues, and tailoring crops and production to specific environments and cultures.

Feedstock costs represent a large part of biorefinery operating costs, therefore availability of an affordable feedstock supply is crucial for the viability of every biomass processing facility (Stokes & R.D. Perlack, 2011). Economics of biomass production vary with location, feedstock type, political policies, current infrastructure, and environmental concerns, and it is seemed as great global market as shown in figure 3 (Demirbas, Balat, & Balat, 2009). Many biofuels may be derived from forestry (thinning and logging), agriculture (residues, non-food, or dedicated biomass crops), municipal organic wastes, algal-based resources,

and by-products or waste products from agro-industry, feed and food industry, and food services (Hughes et al., 2013; Moshkelani, Marinova, Perrier, & Paris, 2013). A hot-spot factor is to identify biomass resources that are sustainable because they require minimal water, fertilizer, land use, and other inputs (D'Avino et al., 2015; Spugnoli, Dainelli, Avino, & Mazzoncini, 2012). Biorefineries feedstocks must be high in energy content, be easy to obtain in great quantities, and be tractable to the conversion processes. There are several researches in progress on technologies to deliver high-quality, stable, and infrastructure-compatible feedstocks from diverse biomass resources.

Figure 3. Impact of sustainable biomass in socio-economic context of the United States of America.



Although sufficient biomass supply is potentially available in various zones, continued improvements in biomass feedstocks worldwide are required to achieve viable third-generation biorefineries around the world. Feedstock production improvements should include: maximizing yield (mainstream and downstream), nutrient (Nitrogenous, Phosphorus, and Potassium), water efficiency, introduction of alternative crops, and sustainability (de Jong & Jungmeier, 2015; Lloveras, Santiveri, & Gorchs, 2006; Lokesh, Sethi, Nikolaidis, Goodger, & Nalianda, 2015). Screening of plant species and plant breeding is critically important to increase efficiency of biomass production while minimizing inputs, maintaining soil fertility, managing water balance, and controlling invasiveness (Guevara & Ramírez, 2015). Knowledge of how to estimate the biomass production potential and to evaluate the impacts and sustainability of production in each location are required.

Improvements in organization include increasing efficiency of harvest, addressing the issue of seasonality to provide continuous supply, and ensuring that biomass cultivation helps drive regional or local development (Hughes et al., 2013). Costs in transporting biomass to the biorefinery can be reduced by using optimized harvesting equipment, appropriate preparation for shipment, and efficient collection, storage, and transfer networks, especially for multi-feedstock biorefineries (Gibbons & Hughes, 2011; Hughes et al., 2013). Processing improvements include optimizing the composition and properties of biomass for handling and transport to meet downstream quality requirements, along with imparting traits such as greater digestibility for ease of conversion or introducing new biomass that can be more feasible to use into biorefinery (Demirbas et al., 2009).

New technologies are reducing the cost of preparing biomass for conversion. Each step of the preparation is designed to develop next-generation feedstocks. Mechanical treatments reduce the size of the feedstock, providing fractionation and separation. Thermal and chemical processes control moisture content, remove contaminants, and improve digestibility and stability to reduce fouling in process equipment (Böhme, Kampf, Lebzien, & Flachowsky, 2005; Krohn & Fripp, 2012; Mehta & Anand, 2009; Zhang, Hui, Lin, & Sung, 2016). Processed and non-processed biomass is typically blended in specific proportions, often with additives to improve conversion efficiency or process effectiveness.

In context of biorefineries and effective use of biomass, third generation biofuel has only recently entered the mainstream it refers to biofuel derived from algae. Previously, algae were lumped in with second generation biofuels (Agusdinata, Zhao, Ileleji, & DeLaurentis, 2011). However, when it became apparent that algae are capable of much higher yields with lower resource inputs than other feedstock (using molecular tools), many suggested that they be moved to their own category (algae biorefineries or third specialized biorefinery). As we will demonstrate, algae provide several advantages, but at least one major shortcoming that has prevented them from becoming a runaway success (Hughes et al., 2013). When it comes to the potential to produce biofuel, no feedstock can compete algae in terms of quantity, manipulability, or diversity. Moreover, the diversity of fuel that algae can produce results from two remarkable characteristics of them. First, algae produce an oil that can easily be refined into diesel or even certain components of gasoline or jet fuel (Demirbas et al., 2009). More importantly, however, is a second property in it can be genetically manipulated to produce everything from ethanol and butanol to even gasoline and diesel fuel directly and efficiently (Gibbons & Hughes, 2011; Hughes et al., 2013).

Butanol is an alcohol of great interest because this alcohol is exceptionally like gasoline. In fact, it has a nearly identical energy density to gasoline and an improved emissions profile (Visioli, Enzweiler, Kuhn, Schwaab, & Mazutti, 2014). Until the advent of GMO algae, scientists had a great deal of difficulty producing butanol. Now, several commercial-scale facilities have been developed and are on the brink of making butanol and more popular biofuel than ethanol because it is not only similar in many ways to gasoline, but also does not cause engine

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damage or even require engine modification the way ethanol does (Hughes et al., 2013; Qiaozhen et al., 2009).



Figure 4. Algae biorefinery system (taken from www.algaebiofueltech.com)

#### 2.1.3. Transesterification of oils and fats

Transesterification has been used for more than a decade to produce biodiesel from plant or animal-derived lipids. Any feedstock that contains free fatty acids and/or triglycerides such as vegetable oils, waste oils, animal fats, and waste greases can be converted to biodiesel. However, the product must meet stringent quality standards (Boateng, Mullen, & Goldberg, 2010; Ilkiliç, Aydin, Behcet, & Aydin, 2011). Therefore, standards such as ASTM D6751 in the United States and EN 14214 in Europe have been implemented to ensure that only high-quality biodiesel reaches consumers and industry in general. Acquisition of refined commodity oils such as soybean oil, rapeseed oil or Camelina oil may account for more than 80% of the cost to produce biodiesel (Agusdinata et al., 2011; Mehta & Anand, 2009). Consequently, inexpensive, non-food feedstocks are critically important to improve process economics (i.e. *Falseflax (Camelina*)

sativa), Safflower (Carthamus tinctorius), Crambe (Crambe abyssinica) AND Flax (Linum usitatissimum)).

Such low-value feedstocks often contain contaminants such as moisture and free fatty acids that render them incompatible with simple, homogeneous, alkaline-catalyzed transesterification (Ilkiliç et al., 2011; Krohn & Fripp, 2012; Zhang et al., 2016). In these cases and whether there is no choice, any of these alternative methods can be useful such as: heterogeneous acid catalysis are needed for efficient conversion to biodiesel (Polshettiwar & Varma, 2010), isothermal pyrolysis (Boateng et al., 2010), pre-hydrogenization of fatty acid (Mihaela, Josef, Monica, & Rudolf, 2013; W.-C. Wang, 2016) and so on.

Figure 5. Biodiesel scheme as a fatty acid methyl ester (FAME). Taken from (http://www.enerfish.eu/p-techno-techno\_id-2/fish-oil-to-biodiesel.html, august 2017)



Ready-for-use biodiesel

An economic comparison between different conversion methods utilizing lowvalue feedstocks revealed that the heterogeneous acid catalyst process had the lowest total capital investment and manufacturing (Pradhan et al., 2008). For biodiesel to expand and mature in the market many key issues must be addressed, such as improving production efficiency through development of costeffective catalysts capable of converting low-quality feedstocks into biodiesel, enhancing availability of low cost feedstocks, and managing agricultural land and water. In addition, biodiesel will require continuous improvement in producing cleaner emissions and reducing environmental impacts, although some of these issues are addressed by after-treatment technologies such as exhaust gas recirculation and selective catalytic reduction (Naik et al., 2010; Visioli et al., 2014).

#### 2.1.4. Bio-jet fuel production

The European Commission, in collaboration with leading European airlines (KLM, AirFrance, Iberia, Lufhtansa and others), launched the European Advanced Biofuels Flightpath (http://ec.europa.eu/energy/en). The EU Biofuels Flightpath set a target of two Million of metric tons per year of bio-jet fuels by 2020, which is approximately 4% of total jet fuel use in Europe (International Air Transport Association (IATA) 2013); see table 1 to more information. Twenty-Five European Union (EU) countries were expected to meet their 2013-2014 provisional renewable energy targets, and the projected share of renewable energy in the gross final energy consumption was 15.3% in 2014 (European Commission 2015).

Several reports addressed a variety of the jet fuel volumetric goals as well as the blending ratio of biofuels with conventional jet fuels, despising the type of jet fuel (Type A or Type B). Analysis suggests that a viable market for biofuels can be maintained when as little as 1% of world jet fuel supply is substituted by a biofuel (Air Transportation Action Group 2011), with aggregation of higher blending ratio for future years, such as 25% by 2020, 30% by 2030, and 50% by 2040 (Air

Transportation Action Group 2009). The substitution of fossil jet fuels effort targets at a 5% replacement in 2018 (USDA 2012). For instance, based on the upper estimate of jet fuel demand, it is generically estimated that between 35%– 100% of global jet fuel demand could be provided by biofuel by 2050 (Bauen, Howes, et al. 2009). EU is projecting low-carbon sustainable fuels in aviation to reach 40 % by 2050 (European Commission 2011). The volumetric targets in the most recent publications or reports are more conservative and are moved from volumetric targets to a GHG emission reduction target of a 50% reduction in carbon emissions by 2050 relative to a 2005 baseline (IATA 2015).

Feedstock costs contribute the most to the overall biofuel production cost. Rising prices for food and feed, surface transportation, and power generation are sources of increasing demand on energy crops (a plant used to produce biofuels or to generate electricity, heat or any other form of energy) and one of the reasons for increasing feedstock prices (W. Wang et al., 2016). Appropriate plantation, cultivation, and harvesting are required before the feedstocks are processed into fuel, in this case non-food cops, multi-proposes crop, and residual biomass are the optimal candidates (Cardone et al., 2003; W.-C. Wang, 2016). Estimates show that 8% of U.S. energy crop and residue resources would be required to fully supply the biojet fuel demand in 2050 (Agusdinata et al., 2011; W. Wang et al., 2016). Potential feedstocks for producing biojet fuel are classified as:

- oil-based feedstocks, such as vegetable oils, waste oils, algal oils, and pyrolysis oils;
- solid-based feedstocks, such as lignocellulosic biomass (including wood products, forestry waste, and agricultural residue) and municipal waste (the organic portion) (Agusdinata et al., 2011; Carlsson, 2009; W. C. Wang & Tao, 2016); or
- gas-based feedstocks, such as biogas and syngas. The key to the successful implementation of bio-jet fuel is the availability of feedstock at a large and sustainable scale and low price. (R. A. Lee & Lavoie, 2013; Lokesh et al., 2015).

International Airline Companies /Manufacturers Category Pathways Companies Agencies Terrabon/MixAlco; Ethanol-to-Jet Defense Advanced Boeing, Virgin Atlantic Lanza Tech/Swedish **Research Projects** Alcohol-to-Biofuels; Jet Coskata Agency, FAA (ATJ) U.S. Navy/NAWCWD, Butanol-to-Jet Gevo; Byogy; Continental Airlines; United Airlines Albemarle/Cobalt; AFRL, DLA, USAF Solazyme UOP; SG Biofuels; Hydroprocessed U.S. Navy, USAF, Boeing, Lufthansa, Virgin Atlantic, Virgin AltAir Renewable Jet Fuels; Agrisoma Netherland Air Force, Blue, GE Aviation, Air New Zealand, Rolls-(HRJ) Biosciences; Neste Royce, Continental, CFM, JAL, Airbus, KLM, NASA, Dutch Military, Oil; Pratt & Whitney, Air China, TAM Airlines, PetroChina; Sapphire EADs let Energy, Oil-to-Jet Blue Airways, IAE, United Airlines, Air Syntroleum/Tyson (UTJ) Food; PEMEX ; ASA France, Finnair, Air Mexico, Thomson Airways, Porter Airlines, Alaska Airlines, Horizon Air, Etihad Airways, Romanian Air, Bombardier Applied Research FAA CLEEN, NRC Catalytic Rolls-Royce, Pratt & Whitney Assoc., Aemetis/Chevron Hydrothermolysis Canada, AFRL Lummus (CH) Global U.S. DOE, U.S. DOD, FT Synthesis Syntroleum; SynFuels; Qatar Airways, United Airlines, Airbus, Rentech; Shell; Solena USAF, Ontario British Airways government Gas to Jet Gas Coskata; INEOS (GTJ) N/A Virgin Atlantic Fermentation Bio/Lanza Tech; Swedish Biofuels Catalytic Virent/Shell, Virdia AFRL, U.S. DOE N/A Upgrading of Sugar to Jet Sugar to Jet Amyris/Total, (STJ) Direct Sugar U.S. Navy, FAA Boeing; Embraer; Azul Airlines; GE; Trip Solazyme, LS9 Airlines Biological to Hydrocarbons

Table 1. Summary of the principal Jet Fuel Production Pathways modified from (W. Wang et al., 2016)

# 2.1.5. Plant oil to Bio-jet fuel transformation process

Oil-to-Jet (OTJ) Fuel has three processes classified into the OTJ conversion pathway:

- hydroprocessed renewable jet (HRJ, also known as hydroprocessed esters and fatty acids or HEFA);
- ii) catalytic hydrothermolysis (CH, also termed hydrothermal liquefaction); and
- iii) pyrolysis (also known as hydrotreated depolymerized cellulosic jet (HDCJ)).

Actually, only biofuels from the HRJ pathway have been approved for blending and have a defined ASTM specification (International Air Transport Association 2010). Oil-derived jet fuels must compete with biodiesel and hydroprocessed renewable diesel for feedstock availability. In this dissertation, the feedstocks considered for OTJ conversion pathways is plant oils produced by Camelina, Flax, Safflower and Crambe.

Plant oils as part of various promising feedstocks are becoming a great alternative to green diesel and bio-jet fuels production, plant oils such as: Canola, Soybean, Camelina, Cartamo, Rapeseed, Palm oils, Corn oil and so on (Li & Mupondwa, 2014; Miller & Kumar, 2013). Soybean oil has been used extensively in the United States for biodiesel production, using 27% (in 2013) and 23% (in 2014) of total soybean oil production (U.S. Department of Agriculture 2015; U.S. Energy Information Administration 2015). Rapeseed oil is the main feedstock used for biodiesel production in Europe, with approximately 850,000 metric tons used in 2014 (Krautgartner et al., 2015). Palm oil consumed in Europe is imported, mainly from Indonesia, and its consumption for biodiesel production is estimated as 1,450 metric tons in 2014 (Boateng et al., 2010; Carlsson, 2009).

Biodiesel production has expanded based on the abundant palm oil resource in Southeast of Asia. However, the use of Soybean, Palm, Camelina, Cartamo, Sunflower and Rapeseed oils as bio-jet fuel feedstocks should lead to a large uncertainty in the amount of Green House Gases (GHG) emissions due to direct or indirect land use change, N-fertilizer production and application, and N<sub>2</sub>O emission to air (D'Avino et al., 2015; Pradhan et al., 2008; Spugnoli et al., 2012). Palm oil use for biodiesel production is expected to be cut in the European Union and United States, according to EPA definition, as it is not suitable for addition to the renewable fuel program due to high GHG emissions (Krautgartner et al., 2015; W.-C. Wang, 2016).

Nowadays, bio-jet fuels derived from plant oils such as camelina and jatropha, algae oils, and waste cooking oils have been tested in commercial (IATA 2010) and military (W. Wang et al., 2016) flights. Camelina is a short-season crop cultivated in the temperate climate zone. Interest in camelina has recently been raised mainly due to the need for easy-to-grow oilseed crops for potential non-food agricultural systems. In a study performed by Shonnard et al., HRJ fuel derived from camelina through Honeywell Green Jet Fuel technology has been shown to not only meet stringent engine fuel and performance specifications but also reduce environmental emissions, that is in concordance with other studies (Krohn & Fripp, 2012; Li & Mupondwa, 2014; Lokesh et al., 2015).

Jatropha has higher oil yield than many other oil-yielding crops. In humid regions or under irrigated conditions, the Jatropha plant can be grown year-round. Jatropha is a promising raw material for biofuels production because the seed oil content is potentially high, at 35%–55% of the seed dry weight (Kasim & Harvey, 2012). Additionally, seed shells of Jatropha have a high energy value (18–19 MJ/kg) (Lokesh et al., 2015; W.-C. Wang, 2016). The seed shells can be converted to value-added co-products compared to algae and palm after oil extraction. Jatropha oil has been a subject of interest, particularly in the biodiesel production area, although there is minimal evidence to show that it will become

an energy resource on a global scale (Kasim & Harvey, 2012; W. Wang et al., 2016)

Algal biofuel has attracted the interest of researchers and entrepreneurs for several reasons (Agusdinata et al., 2011; Herrero, Sánchez-Camargo, Cifuentes, & Ibáñez, 2015; W. C. Wang & Tao, 2016):

- i) algae have high productivity per acre and year-round production;
- algal cultivation requires less freshwater than terrestrial crops and can use a variety of water sources including fresh, brackish, saline, and wastewater;
- iii) algae can be cultivated on non-arable land;
- iv) algae have rapid growth potential and high oil content (20%–50% dry cell weight);
- v) nutrients such as nitrogen and phosphorus for growth can be obtained from wastewater;
- vi) various valuable co-products, such as proteins and residual biomass left after oil extraction potentially can be used as feed or fertilizer;
- vii) hydrogen can be produced photobiologically from microalgae; and (8) the potential GHG reduction relative to other plant oils.

Three algae production technologies-photoautotrophic, heterotrophic, and mixotrophic-have developed (Brennan Owende been and 2010). Photoautotrophic production can occur in either open ponds or closed photobioreactor systems. Open pond systems have the advantages of cheaper algae production cost (\$10.6/gal in 2011 U.S. dollars) and low energy input, but they have poor productivity and require large areas of land (Davis, Aden, et al. 2011). There are still inconsistencies in the production rates reported in literature, ranging from 10–69 g/m2/day for an open pond system (Brennan and Owende 2010). Closed photobioreactor systems have a higher algae production cost of \$22.4/gal in 2011 U.S. dollars, high energy input, and relatively higher productivity of 1.25 kg/m 3/day on a volume basis (Davis, Aden, et al. 2011). The algal biomass is harvested through bulk harvesting and concentrating. The harvesting process includes flocculation, filtration, flotation, and centrifugal sedimentation steps, which are crucial to the economic production of micro-algal biomass. The dehydration or drying step is commonly used after the harvesting process for thickening. Various drying technologies used for this purpose are sun drying, low-pressure shelf drying, spray drying, drum drying, fluidized bed drying, freeze drying, and Reactance Window technology drying (Brennan and Owende 2010). Freeze drying is expensive, but it makes oil extraction easier than other technologies (Grima, Medina, et al. 1994).

Another technology available is pyrolysis, that is a process that heats biomass without oxygen either in a fast or slow process, produces pyrolysis gas (also called syngas), biochar, and pyrolysis oil (also called bio-oil) (Angin, 2013; R. A. Lee & Lavoie, 2013). Pyrolysis oil is a mixture of oxygenated organic species containing carbons ranging C1-C21. Some examples of the carbon chain length of pyrolysis oil are shown in literature (Harris, Lawburgh, Lawburgh, Michna, & Gent, 2014; Hasan Khan Tushar et al., 2012; W.-C. Wang, 2016; Wright, Daugaard, Satrio, & Brown, 2010). Although pyrolysis oil is very different from either vegetable oil or algal oil, it can be refined similarly into renewable gasoline, diesel, or jet. In a literature review, the production cost of bio-oil was shown to range from \$0.5/gal to \$2.0/gal in 2011 dollars in United States (Badger, Badger, Puettmann, Steele, & Cooper, 2011; Wright et al., 2010). The sale of co-product biochar potentially reduces the production cost of bio-oil by up to 18% depending on the biochar market, with an assumed feedstock (wood chips) cost of \$25/wet ton (or \$50/dry ton) (Badger, Badger, et al. 2011).

When processing oils, the fatty acid profile is an important issue. For instance, a greater hydrogen supply is needed if more unsaturated fatty acids are present in the oil (Bondioli, Folegatti, Lazzeri, & Palmieri, 1998). Vegetable oils, waste cooking oil, and algal oil are in the diesel fuel range C16–C22. Oleic acid is a predominant proportion of vegetable oils. Oils from algae, especially, contain a

significant amount of eicosapentaenoic acid. High-chain-length oils can be broken down to small molecules to produce jet fuels, but the overall yield will be reduced with increasing production of co-products (Man, Wong, & Yung, 2012; W. C. Wang & Tao, 2016). If starting from small molecules, the target jet fuel product yield will be high with fewer co-products produced. There is a tradeoff between main product (jet fuel) and value-added co-product production ratios.

## 2.1.6. Hydro-processed renewable jet fuel (HRJF)

Both HRJF and catalytic hydrothermolysis (CH) processes employ triglyceridebased feedstocks (fatty acids), but the free fatty acids (FFAs) are produced through different pathways. FFAs in the HRJ process are made by propane cleavage of glycerides, whereas in the CH process, FFAs are produced by thermal hydrolysis (W.-C. Wang, 2016). In the pyrolysis process, the bio-oil is produced via biomass feedstock pyrolysis Hydrotreating for HRJF, CH, and several kinds of pyrolysis are very similar.

HRJF conversion technology is at a relatively high maturity level and is commercially available. It was recently used to produce jet fuel for commercial and military flights (Lokesh et al., 2015). HRJF fuel is equivalent to conventional petroleum in properties, but has the advantages of higher cetane number, lower aromatic content, lower sulfur content, and potentially lower GHG emissions (Lokesh et al., 2015; Zhang et al., 2016). Over the past 60 years, a large variety catalytic hydrogenation, deoxygenation, hydroisomerization, of and hydrocracking processes have been successfully developed and commercialized. A representative process flow diagram is shown in Figure 2. Renewable fats and oils that have different degrees of unsaturation require a hydrogenation process to saturate the double bonds completely (Kalnes, McCall, & Shonnard, 2010).
First, catalytic hydrogenation could be used to convert liquid-phase unsaturated fatty acids or glycerides into saturated ones with the addition of hydrogen (Kalnes et al., 2010). The next step is to cleave the propane and produce three moles of FFAs (Pearlson 2007). The glycerol portion of the triglyceride molecule is converted into propane by adding hydrogen (H<sub>2</sub>). An alternative route to convert the glycerides to FFAs is thermal hydrolysis (Wang, Turner, et al. 2012). Oils and fats that contain mostly triglycerides are converted into three moles of FFAs and one mole of glycerol by processing the feedstocks with three moles of water. The hydrogen ion from the water is attached on the glycerol backbone and forms one mole of glycerol, where the hydroxyl ion from the water is added to the ester group and produces three moles of FFAs. High temperature (250°C-260°C) is required for water to dissolve in the oil phase. High pressure is also necessary to maintain the reactants in liquid phase. The co-product glycerol has many pharmaceutical, technical, and personal care product applications. The glycerol purification process is energy intensive, adding cost to overall process, but might be offset by glycerol selling value (Yang, Hanna, et al. 2012).

Figure 6. Hydroprocessed renewable jet (HRJ) process taken from (W.-C. Wang, 2016)



To meet the jet fuel specification, the produced bio-jet fuel must have not only a high flash point, but also good cold flow properties. Therefore, it is required to hydrocrack and hydroisomerize the normal paraffins produced from deoxygenation to a SPK product with carbon chains ranging from C9 to C15 (Kalnes et al., 2010). The cracking and isomerization reactions are either concurrent or sequential (de Jong & Jungmeier, 2015; Fatih Demirbas, 2009; Kalnes et al., 2010). Studies have shown that isomerization of straight-chain alkanes occurs first, and cracking is a sequential reaction. The isomerization process takes the straight-chain hydrocarbons and turns them into the branched structures to reduce the freeze point to meet the jet fuel standard (Gary, Handwerk, et al. 2007). It is accompanied by a hydrocracking reaction, which results in yield from the isomerized species.

The hydrocracking reactions are exothermic and result in the production of lighter liquids and gas products. They are relatively slow reactions; thus, most of the hydrocracking takes place in the last section of the reactor. The hydrocracking reactions primarily involve cracking and saturation of paraffins. Overcracking will result in low yields of bio-jet fuel range alkanes and high yields of light species ranging from C1 to C4, and naphtha ranging from C5 to C8(Boateng, Mullen, & Goldberg, 2010; Zhang, Hui, Lin, & Sung, 2016) . Both are out of jet fuel range and have lower economic value than diesel or jet fuel.

Bifunctional catalysts containing metallic sites for process of hydrogenation or dehydrogenation and acid sites for selective isomerization via carbynium ions could be used in isomerization (Giannetto, Perot, et al. 1986). In a typical isomerization reaction, normal paraffins are dehydrogenated on the metal sites of the catalyst and reacting on the acid sites to produce olefins protonate with formation of the alkyl-carbynium ion. The alkyl-carbynium ion is rearranged to mono-branched, di-branched, and tri-branched alkyl-carbynium ions on the acid site. The branched alkyl-carbynium ions are deprotonated and hydrogenated to produce the corresponding paraffins (Park and Ihm 2000). The choice of catalyst will result in variation of cracking at the end of the paraffin molecule and,

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therefore, adjust the yield of jet—fuel-range product (Kalnes, McCall, et al. 2010). The hydro isomerization and hydrocracking processes are followed by a fractionation process to separate the mixtures to paraffinic kerosene (HRJ SPK), paraffinic diesel, naphtha, and light gases.

## 2.2. Non-conventional oleaginousness description

## 2.2.1. Falseflax (Camelina sativa)

Falseflax, Gold of pleasure or Camelina are the common names of *Camelina sativa (C. sativa),* in table 2 is listed its taxonomy. Camelina has been traditionally cultivated as an oilseed crop to produce vegetable oil and animal feed (Li & Mupondwa, 2014; Szumacher-Strabel et al., 2011). Several archeological evidences show it has been grown in Europe for at least 3,000 years. Until the 1940s, camelina was an important oil crop in eastern and central Europe, and currently has continued to be cultivated in a few parts of Europe for its seed oil (Fleenor, 2011). Camelina oil was used in oil lamps (until the modern harnessing of natural gas, propane, and electricity) and as an edible false flax oil.

Camelina is a short-season crop (85–100 days) and grows well in the temperate climate zone in light or medium soils. Camelina is generally seeded in spring from March to May, but can also be seeded in fall in mild climates. A seeding rate of 3–4 kg/ha is recommended, with a row interval of 12 to 20 cm. With high seeding rates, these independently non-competitive seedlings become competitive against weeds because of their density. The seedlings are early emerging and can withstand mild frosts in the spring (Fleenor, 2011; Krohn & Fripp, 2012). Minimal seedbed preparation is needed to establish camelina.

Table 2. Taxonomy of Camelina sativa. Taken from USDA web page.

Rank	Scientific Name and Common Name
Kingdom	Plantae – Plants
Subkingdom	Tracheobionta – Vascular plants
Superdivision	Spermatophyta – Seed plants
Division	Magnoliophyta – Flowering plants
Class	Magnoliopsida – Dicotyledons
Subclass	Dilleniidae
Order	Capparales
Family	Brassicaceae / Cruciferae – Mustard family
Genus	Camelina Crantz – false flax
Species	Camelina sativa (L.) Crantz – false flax

Commonly, camelina does not need any field interventions. However, perennial weeds may be difficult to control. Some specialized oilseed herbicides can be used on it. No insect has been found to cause economic damage to camelina. Camelina needs little water or nitrogen to flourish; it can be grown on marginal agricultural lands. Fertilization requirements depend on soils, but are generally low. It may be used as a rotation crop for wheat and other cereals, to increase the health of the soil. Camelina can also show some allelopathic traits, and it can be grown in mixed crop with cereals or legumes. Camelina is harvested and seeded with conventional farming equipment, which makes adding it to a crop rotation relatively easy for farmers who do not already grow it (Fleenor, 2011; Tuziak, Rise, & Volkoff, 2014). Seed yields vary depending on conditions ranging 500-2700 kg/ha.

The state of Montana, in The United States, has recently been growing more camelina for its oil potential as a biofuel, bioplastic feedstock and bio-lubricant. Plant scientists at the University of Idaho, Washington State University, and other institutions also are studying this emerging biodiesel produced from camelina oil.

Studies have shown camelina-based jet fuel reduces net carbon emissions by about 80% (Agusdinata et al., 2011; Krohn & Fripp, 2012; Lokesh et al., 2015; Righini, Zanetti, & Monti, 2016).

Continental Airlines, was the first commercial airline to test a 50:50 blend of bioderived "green jet" fuel and traditional jet fuel in the first demonstration of the use of sustainable biofuel to power a commercial aircraft in North America (IATA2015). The demonstration flight, conducted in partnership with Boeing, GE Aviation/CFM International, and Honeywell's UOP, marked the first sustainable biofuel demonstration flight by a commercial carrier using a two-engine aircraft: a Boeing 737-800 equipped with CFM International CFM56-7B engines. Continental ran the blend in Engine No. 2. During the two-hour test flight, Continental pilots engaged the aircraft in several normal and non-normal flight maneuvers, such as mid-flight engine shutdown and restart, and power accelerations and decelerations.

Camelina has been approved as a cattle feed supplement by Food and Drugs Administration (FDA) as well as an ingredient (up to 10% of the ration) in broiler chicken feed and laying hen feed (Cherian, 2012; Frame, Palmer, & Peterson, 2007; Pekel, Kim, Chapple, & Adeola, 2015) and trout and salmonids feed (Nasopoulou & Zabetakis, 2012; Tuziak et al., 2014). Camelina meal, the byproduct of camelina when the oil has been extracted, has a significant crude protein content. Feeding camelina meal has significantly increased omega-3 fatty acid concentration in breast and thigh meat of turkeys compared to control group (Cherian, 2012; Frame et al., 2007). Camelina oil and meal have also been investigated as a sustainable lipid source to fully replace fish oil and to replace fish meal in diets for farmed Atlantic salmon, Rainbow Trout, and Atlantic cod (Boissy et al., 2011; Fraser et al., 2016; Hixson, Parrish, & Anderson, 2014) . However, various antinutritional factors are present in camelina meal and can affect its use as livestock feed. Considering this, FDA has recommended to use cold pressed camelina meal in animal feed until 10% w/w, on the other hand, The Canadian Food Inspection Agency has approved feeding cold-pressed nonsolvent extracted Camelina meal to broiler chickens at up to 12% inclusion.

## 2.2.2. Safflower (Carthamus tinctorius)

Safflower is one of humanity's oldest crops and its taxonomy is presented in table 3. According to several published papers (Flemmer, Franchini, & Lindstr??m, 2015; Y. C. Lee, Oh, Chang, & Kim, 2004; Pearl & Burke, 2014), chemical analysis of ancient Egyptian textiles dated to the Twelfth Dynasty identified dyes made from safflower, and garlands made from safflowers were found in the tomb of the pharaoh Tutankhamun. Traditionally, the crop was grown for its seeds, and used for coloring and flavoring foods, in medicines, and making red (carthamin) and yellow dyes, especially before cheaper aniline dyes became available (Clementi, Basconi, Pellegrino, & Romani, 2014; Pearl & Burke, 2014).

Table 3.	Taxonomy c	of Carthamus	tinctorius.	Taken f	from USDA	web page.
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Rank	Scientific Name and Common Name
Kingdom	Plantae – Plants
Subkingdom	Tracheobionta – Vascular plants
Superdivision	Spermatophyta – Seed plants
Division	Magnoliophyta – Flowering plants
Class	Magnoliopsida – Dicotyledons
Subclass	Asteridae
Order	Asterales
Family	Asteraceae/Compositae – Aster family
Genus	Carthamus L. – distaff thistle
Species	Carthamus tinctorius L. – safflower

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For the last fifty years or so, the plant has been cultivated mainly for the vegetable oil extracted from its seeds. Safflower seed oil is flavorless and colorless, and nutritionally like sunflower oil. It is used mainly in cosmetics and as a cooking oil, in salad dressing, and to produce margarine (Clementi et al., 2014; Y. C. Lee et al., 2004).

There are two types of safflower that produce different kinds of oil: one high in monounsaturated fatty acid (oleic acid) and the other high in polyunsaturated fatty acid (linoleic acid). Currently the predominant edible oil market is for the former, which is lower in saturated fats than olive oil. The latter is used in painting in the place of linseed oil, particularly with white paints, as it does not have the yellow tint which linseed oil possesses. Oils rich in polyunsaturated fatty acids, notably linoleic acid, are considered to have some health benefits (Clementi et al., 2014; Mihaela et al., 2013). One human study compared high-linoleic safflower oil with conjugated linoleic acid, showing that body fat decreased, and adiponectin levels increased in obese women consuming safflower oil.

## 2.2.3. Crambe (Crambe abyssinica)

Crambe, which is closely related to rapeseed and mustard, is an erect annual herb with numerous branches that grows to a height of 50 to 105 cm, its taxonomy is shown in table 4. Under stress conditions plants may develop long tap roots, which later become conical. The leaves are oval shaped, but asymmetric (Bondioli et al., 1998; Righini et al., 2016). Crambe initially produces numerous small, white flowers in a compact group. The spherical fruits bear one seed each. The seed remains in the pod or hull at harvest. Mature fruits are dry, persistent, and indehiscent. They vary in color from light green to light brown (Zhu, 2016).

The oil extracted from Crambe seed is used as an industrial lubricant, a corrosion inhibitor, and as an ingredient in the manufacture of synthetic rubber (Bondioli et al., 1998; Carlsson, 2009; Lazzeri, Mattei, Bucelli, & Palmieri, 1997). The oil

contains from 50% to 60% erucic acid (C22), a long chain fatty acid, which is used in the manufacture of plastic films, plasticizers, nylon, adhesives, and dielectric oils (Kammann & Phillips, 1985; Vargas-Lopez, Wiesenborn, Tostenson, & Cihacek, 1999). Crambe is being promoted as a new domestic source of erucic acid, which has primarily come from imported rapeseed oil. Supplies of industrial rapeseed are less-plentiful since the development of varieties (Canola) that have no erucic acid content.

Defatted Crambe seed meal can be used as a protein supplement in livestock feeds. The meal contains 25% to 35% protein when the pod is included and 46% to 58% protein when the pod is removed. It has a well-balanced amino acid content and has been approved by the FDA for use in beef cattle rations for up to 5% of the daily intake (Böhme et al., 2005; Carlson, Baker, & Mustakas, 1985; Mendonça, Lana, Detmann, Goes, & Castro, 2015).

#### Table 4. Taxonomy of Crambe abyssinica. Taken from USDA web page.

Rank	Scientific Name and Common Name		
Kingdom	Plantae – Plants		
Subkingdom	Tracheobionta – Vascular plants		
Superdivision	Spermatophyta – Seed plants		
Division	Magnoliophyta – Flowering plants		
Class	Magnoliopsida – Dicotyledons		
Subclass	Dilleniidae		
Order	Capparales		
Family	Brassicaceae/Cruciferae – Mustard family		
Genus	Crambe L. – crambe		
Species	Crambe abyssinica Hochst. ex R.E. Fries – crambe		

The meal has not been approved for non-ruminant feed because it may contain glucosynolates, which may be broken down in digestive systems to form harmful products that can cause liver and kidney damage, and appetite depression (Daubos et al., 1998). Untreated, oil-free Crambe meal may contain up to 10% thioglucosides, which are toxic to non-ruminant animals, such as hogs and chickens. However, subjecting whole seed to moist heat before processing can deactivate the enzyme, and the glucosynolates remain intact through the oil extraction process (Daubos et al., 1998; Mendonça et al., 2015).

### 2.2.4. Flax (Linum usitatissimum)

*L. usitatissimum L.* is a species of the family Linaceae (see table 5). It is an erect, herbaceous annual which branches cymosely above the main stem (Morris, 2007). Two types of *L. usitatissimum* are cultivated (Lloveras et al., 2006; Morris, 2007):

i) the linseed type, grown for oil extracted from the seed, is a relatively short plant which produces many secondary branches compared to;

ii) the flax type, grown for the fiber extracted from the stem, which is taller and is less branched.

*L. usitatissimum* has a short tap root with fibrous branches which may extend 90 - 120 cm in light soils. Leaves are simple, sessile, linear-lanceolate with entire margins, and are borne on stems and branches. The inflorescence is a loose terminal raceme or cyme. Flowers are borne on long erect pedicels, are hermaphrodite, hypogenous and are composed of five sepals, five petals (blue), five stamens, and a compound pistil of five carpels each separated by a false septum. The fruit is a capsule, composed of 5 carpels and may contain up to 10 seeds (Hall, Booker, Siloto, Jhala, & Weselake, 2016; Morris, 2007). The seed is oval, lenticular, 4-6 mm long with a smooth, shiny surface, brown to light-brown

in color. Seeds contain 35-45% oil and 20-25% protein (Lloveras et al., 2006; Matthäus & Zubr, 2000; Morris, 2007).

Canada is a major producing country along with Argentina, India, the USA, and Russia; most Canadian flaxseed is exported as linseed. Traditionally, the oil pressed from the seed (linseed oil) has been used for a variety of industrial purposes and the oil-free meal could be fed to livestock (boiling with water is advised to counteract the effect of the cyanogenetic glycoside linamarin). Recently, plant breeders have been successful in developing a low linolenic-acid edible oil flax for human consumption. In addition to usage of seed for industrial purposes, whole flaxseed is used extensively in baked goods in Europe (Jhala & Hall, 2010; Lloveras et al., 2006; Morris, 2007).

#### Table 5. Taxonomy of Linum usitatissimum L. Taken from USDA web page.



# Flax is grown primarily in the three prairie provinces of western Canada, specifically in southern Manitoba, Saskatchewan, and Alberta (Hall et al., 2016; Kissinger, Fix, & Rees, 2007). It grows best on heavy loam soils that retain

moisture well. Because of its limited root system, flax does not grow well on sandy, moisture-limited soils. Flax is moderately tolerant to salinity whether soil nutrients are present at adequate levels and that moisture is not limiting at germination (Hall et al., 2016; Jhala & Hall, 2010; Morris, 2007).

Flax may be grown in rotation with cereals or corn but not following potatoes or sugar beets (because of problems with root diseases) or following a previous flax crop. A three-year period is recommended between flax crops to avoid fusarium wilt. Flax may grow poorly after canola or mustard; control of volunteers may minimize the detrimental effects. Seeding is usually done when soil temperatures are warm (mid-May on the prairies), at a rate of 30 to 40 kg/ha and no deeper than 2.5 to 4 cm. If the seed coat has been damaged at harvest, soil-borne fungi may infect the seed; therefore, seed treatment with a fungicide will increase seedling emergence and vigor. Flax does not require as much fertilizer as cereals but will benefit if nitrogen or phosphorus is limiting (Hall et al., 2016; Yan, Chouw, & Jayaraman, 2014).

For centuries, flax fiber has occupied a prominent place in textile industry. The prehistoric habitants of Lake Dwellers of Switzerland used flax fiber to produce linen. The art of weaving flax fiber to linen may have originated in Egypt because winding-clothes for the bodies of the Pharaohs of Egypt were composed of flax fiber. It was then introduced in India, where, before the use of cotton, linen was worn by many tribes (Jhala & Hall, 2010; Kong, Park, & Lee, 2014). One of the limitations of flax is the separation of best fiber from other stem fibers. Retting traditionally did this; two traditional methods were used commercially to ret flax for industrial grade fibers, water- and dew-retting (Jhala & Hall, 2010).

 Water retting method was discontinued because of the high cost of drying and the pollution from the anaerobic decomposition of flax stem in lakes and rivers. ii) Dew-retting has also limitations including poor quality fiber and is restricted to regions which have appropriate moisture and temperature ranges suitable for retting (Evans, Akin, & Foulk, 2002).

In the 1980s, several efforts were made to overcome these limitations and to develop a new method known as enzyme-retting, replacing the anaerobic bacteria with enzymes (Jhala & Hall, 2010). Attempts were also being made by United States Department of Agriculture (USDA) to develop an enzyme-retting pilot plant method to replace traditional methods of retting, thus producing flax fibers with specific properties for industrial uses (Evans et al., 2002). Advantages of this method may include: reduced retting time, increased yield and consistency, and stability of production and supply.

Fiber obtained from flax is known for its length, strength, flexibility, and fineness; however chemical composition and diameter are also important (Hall et al., 2016). In comparison to industrial wood particles, flax particles were characterized by higher length to thickness and length to width ratios and lower bulk (Jhala & Hall, 2010). The best grades are used for linen fabrics such as damasks, lace, and sheeting. Coarser grades are used for the manufacturing of twine and rope. Flax is a source of industrial fibers and, as currently processed, results in long-line and short fibers. Long line fiber is used in manufacturing high value linen products, while short staple fiber has historically been the waste from long line fiber and used for lower value products like blankets, mats, mattresses, and carpets (Lloveras et al., 2006).

Flax fiber threads are strong enough for preparation of sewing threads, button threads and shoe threads. Linen is also used in making the highest quality handkerchiefs, bedding, curtains, drapery, cushion covers, wall coverings, towels, other decorative materials and materials for suits and traditional dresses in Asia. It can also be used for manufacturing composites such as particleboard

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(Jhala & Hall, 2010). Flax fibers are also becoming an integral part of new composite materials utilized in automobile and constructive industry.

Bio composites made up from the flax fiber based on polyhydroxybutyrate (PHB) polymer could be an eco-friendly and biodegradable alternative to conventional plastics (Morris, 2007; Pil, Bensadoun, Pariset, & Verpoest, 2016). After extraction of bast fiber from flax stem, 80% of the remains fiber can be separated mechanically. This material can be converted into pulp and can be used for manufacturing papers (Camarero et al., 2004; Lloveras et al., 2006). Flax fiber is also a raw material for the paper industry for the use of printed banknotes and paper for cigarettes. There are several advantages of using flax fibers for industrial applications (Hammett et al., 2001; Lloveras et al., 2006; Peng, Zeng, Wang, & Hong, 2015). It is a biodegradable, renewable raw material, nonabrasive. However, for technical uses, the mechanical properties like tensile strength, elastic modules it may not be suitable (Deng et al., 2016; Kong et al., 2014; Lloveras et al., 2006; van der Werf & Turunen, 2008).

### 2.3. Life Cycle Assessment

Life cycle assessments (LCA), until now, have generally been used to analyze the effects that a product, process, or services will have on the environment. Results of an LCA study will let companies and people in general know which aspects of their production are efficient, and where they can improve efficiency to reduce environmental and social impacts. All stages in the life cycle of the product are considered in a LCA, from the mining and extraction of its raw materials, to the shipping, right on to the landfill. Data are not only considered for the initial product, but also for the full life cycles of other materials that are used in the making of the product. Social (S-LCA) and socio-economic life cycle assessments add extra dimensions of impact analysis, valuable information for those who seek to produce or purchase responsibly. (Dreyer, Hauschild, & Schierbeck, 2010; Unep Setac Life Cycle Initiative, 2009).

Figure 7. Cradle to grave LCA (a) and LCA framework according to ISO 1404X family (b) (Anctil & Vasilis, 2012).



One of the complexities of LCA is that it has been applied to different types of decisions, ranging from single products to large scale policy decisions such as whether or not to build a particular power plant instead a biorefinery (Gasol, 2009; Menichetti & Otto, 2009). Although LCA was developed for single products, in recent years there has been a distinct shift in applying it to such larger scale decision contexts (Menichetti & Otto, 2009; Ramachandran, Singh, Larroche, Soccol, & Pandey, 2007). Part of the reason for this shift has been the argument that since LCA is useful for determining the environmental impacts of a product, surely it is useful for determining the environmental impacts of a "product" like a power plant.

This shift in perspective from "conventional" to "unconventional" products has been described as two separate types of LCA:

 Attributional life cycle assessment (focuses on describing the environmentally relevant physical flows to and from a product or process emit). ii) Consequential life cycle assessment (describes how relevant environmental flows will change in response to possible decisions).

Ultimately, the differences between attributional and consequential LCA are the result of the choices made in the aim and scope definition of steps of the LCA process (Brander, Tipper, Hutchison, & Davis, 2008; European Commission -- Joint Research Centre -- Institute for Environment and Sustainability, 2010; Thomassen, Dalgaard, Heijungs, & de Boer, 2008). In consequential LCA, the system boundaries are defined to include the activities contributing to the environmental consequence of the change – regardless of whether or not these changes are within or outside of the cradle-to-grave system being investigated (D'Avino et al., 2015; J. H. Schmidt, 2008).

As a result, the process of system expansion (to avoid or deal with the allocation problem in multi-product systems) is an inherent part of consequential LCA studies. In consequence, consequential LCA includes additional economic concepts like marginal production costs, elasticity of supply and demand, dynamic models (instead of the linear and static models of traditional LCA), etc.(European Environment Agency, 2012; Gasol, 2009) It is typically more conceptually complex and the results obtained are highly sensitive to assumptions made.

Figure 8. Dynamic of Life Cycle Assessment in attributional and consequential points of view. Source taken from <a href="http://www.bioenergyconnection.org/article/life-cycle-analysis-bioenergy-policy">http://www.bioenergyconnection.org/article/life-cycle-analysis-bioenergy-policy</a>.



The failure to identify inadequate implicit assumptions will led to a poor analysis. While attributional LCA uses average data (i.e., data representing the average environmental burden for producing a unit of the good or service in the system), consequential LCA uses marginal data representing the effects of a small change in the output of goods and/or services. Focusing on marginal data narrows the set of data required, since indicators that do not change because of the intervention do not have to be known – which is not the case in attributional LCA (Brander et al., 2008; J. H. Schmidt, 2008; Thomassen et al., 2008). Instead, the challenge in consequential LCA is thoroughly justifying that indicators will not be impacted and thus can be ignored in the analysis.

Taking an example to explain properly LCA. Let us imagine that "XY Inc"—a hypothetical retailer—has requested a LCA of their latest product: a package of colorless shirts. XY Inc. wants to know how this new item will affect its environmental footprint (E-LCA) as a corporation as well as what sort of improvements they can make to the production of the shirts that will reduce emissions and other harmful environmental outputs. Furthermore, "XY Inc" wants to know what sort of social and socio-economic effects these shirts will have on their workers and on the communities where they have shirt factories. As an already established company, XY is legally held to minimum benchmarks for things like workers' rights but they want to take their social responsibility further and need guidance on how to proceed.

The label "Fair Trade" is limited in scope and ignores huge sections of the life cycle reducing its feasibility (Jørgensen, 2013; Weidema, 2005). While the making of shirts may be ethical, the company wants to know if this can be true for "Cradle to Grave" or further "Cradle to Cradle" analysis of production (Braungart, McDonough, & Bollinger, 2007), including phases like shipping, disposal and so on. These specifications and questions will help the analysts focus on finding data relevant to the goals of "XY Inc". They will work in cooperation with the analysts to determine what sort of data will be required to do the study. What kind of emissions to the air, water, or land will the study consider? The list of chemicals released into nature during the production of the shirts, some more potent and detrimental than others. Special attention will probably be paid to outputs like carbon dioxide, nitrogen dioxides and other greenhouse gases. Furthermore, the analysts will inform the stakeholders on which phases of the life cycle of the product might have the greatest share of worker hours and moreover, for which phases of the life cycle the social impacts may be the most important, using additional data (Dreyer et al., 2010; Grießhammer, Benoît, Dreyer, & Flysjö, 2006).

Figure 9. Evolution of categories in time, giving by Bioenergy connection (NGO). Source taken from (http://www.bioenergyconnection.org/article/life-cycle-analysisbioenergy-policy.)



The analyst will consider all the data found on the shirts, considering every piece and process involved in the making of the product, as much as can be acquired. The impacts of the gathering and shipment of raw cotton to a textile company, of refining that cotton into a fabric that can be seen into shirts, the dyeing of the fabric, the stitching, the printing, and addition of those uncomfortable tags that go on the necks of the shirts that say "XY Inc" in little letters—each part is factored in. However, this is just the first step. Analysts then need to consider the impacts of the life cycles of the dyes, threads, and nylon label tags up until the point at which they enter the life cycle of the shirt itself. By the end of the study, analysts will have data that can tell them exactly how much carbon dioxide is produced for each shirt they make. As much as they can, the analysts will also try to find the information on the location where each of the inputs were made and how they were transported. But that is just the easy part. Environmental impacts are much more easily standardized and quantified tan social and socio-economic ones, for obvious reasons (Hauschild, Dreyer, & Jørgensen, 2008; Jørgensen, 2013; Unep Setac Life Cycle Initiative, 2009). Emissions, for example, can be readily measured and given numerical data that can be used over and over. However, Social Life Cycle Assessments (S-LCA) are surely as important as environmental ones (Menichetti & Otto, 2009; Unep Setac Life Cycle Initiative, 2009; Weidema, 2005). How can we proceed to conduct an S-LCA? How do we collect the data? How can we begin to assess and measure the social effects of a T-shirt? How do we define a socially responsible company or practice? How do we bring the results for every phase of the life cycle together? These questions must be answered.

One of the most important issues with S-LCA is keeping consistency among the standards between studies. Even, if its standards can eventually become similar in criteria, differences among studies will always occur. Generally, practitioners of S-LCA will need to incorporate a large share of qualitative data, since numeric information will be less capable of addressing the issues at hand. When numeric data is useful additional data will still be needed to address its meaning: compliance with minimum wage laws does not always mean the wages are livable. Often, data may have to be collected on the spot, since databases for specific social and socio-economic impacts are at a minimum. As one might guess, the current limitations of S-LCA are many. For these reasons, there is no agreement in practitioners of S-LCA. On the other hand, E-LCA is known as a suitable methodology to assess sustainability of great number of items (products).

It is important to estimate environmental and social impacts of these activities in order to make it more affordable throughout technology changes and improvements. However, to make it possible some consideration should be taken. In this particular case, environmental assessment was performed.

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#### 2.3.1. Green House Gases emissions

An estimated 18% of global Green House Gases (GHG) emissions arise from land use change and forestry. These estimates are uncertain and emission estimates range from 2,899 Mt of carbon dioxide to 8,601 Mt (20% of carbon dioxide emissions) (Gallejones, Pardo, Aizpurua, & Del Prado, 2015; Rebitzer et al., 2004; J. H. Schmidt, 2008). Deforestation is by far the largest component of land use changes emissions and, in the land use of tropical forest has changed. Drawing on FAO statistics 19,58% of the deforestation has been influenced by commercial agriculture. The agriculture as a driver can be complex with interaction with other drivers such as road building, logging, primary extraction, manufacturing and population growth.

Most public debate about food and deforestation is focused in direct links between land use change and the food system and today an emerging bioproducts system. Considering the dominance of the tropics in land use change (Lambin et al., 2001), this focuses attention on produce from these regions, particularly soy and beef from South America and palm oil from South-east Asia. This approach to the problem regards deforestation as attributable to USA and EU food consumption when world's consumed food is grown on recently converted land. (Ramankutty, 2007). Considering the Global Warming Potential and other impact categories is necessary to estimate N<sub>2</sub>O production due to N-Fertilizers and residuals during de process.

Estimation of Global Warming Potential (GWP) was developed to allow comparisons of the global warming impacts of different GHG. Specifically, it is a measure of how much energy the emissions of 1 ton of a gas will absorb over a given period, relative to the emissions of 1 ton of carbon dioxide (CO<sub>2</sub>). The larger GWP, the more that a given gas warms the Earth compared to CO<sub>2</sub> over that period. The time usually used for GWPs is 100 years (IPCC). GWPs provide a common unit of measure, which allows analysts to add up emissions estimates of different gases (e.g., to compile a national GHG inventory), and allows

policymakers to compare emissions reduction opportunities across sectors and gases (IPCC, 2006a, 2006c).

Considering the most harmful GHGs, CO<sub>2</sub> has a GWP of 1 regardless of the period used, because it is the gas being used as the reference. CO<sub>2</sub> remains in the climate system for a very long time: CO2 emissions cause increases in atmospheric concentrations of CO<sub>2</sub> that will last thousands of years. Methane (CH<sub>4</sub>) is estimated to have a GWP of 28–36 over 100 years (EPA's U.S. Inventory of Greenhouse Gas Emissions and Sinks uses a different value). CH<sub>4</sub> emitted today lasts about a decade on average, which is much less time than CO<sub>2</sub>. However, CH<sub>4</sub> also absorbs much more energy than CO<sub>2</sub>. The net effect of the shorter lifetime and higher energy absorption is reflected in the GWP. The CH4 GWP also accounts for some indirect effects, such as the fact that CH4 is a precursor to ozone, and ozone is itself a GHG. Nitrous Oxide (N2O) has a GWP 265–298 times that of CO<sub>2</sub> for a 100-year timescale. N<sub>2</sub>O emitted today remains in the atmosphere for more than 100 years, on average. Chlorofluorocarbons hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs), (CFCs), perfluorocarbons (PFCs), and sulfur hexafluoride (SF6) are sometimes called high-GWP gases because, for a given amount of mass, they trap substantially more heat than CO<sub>2</sub>. (The GWPs for these gases can be in the thousands or tens of thousands) (IPCC, 2006b, 2006c, 2006d).

## **CHAPTER 3**

## 3. Methodology

## 3.1. Life cycle assessment framework (ISO 14040)

The International Organization for Standardization identifies four phases for conducting a LCA, those are showed in figure 7(b) (International Organization for Standardization, 2007; Weidema, 2005):

- Goal and Scope (functional unit), where the reasons for carrying out the study and its intended use are described and where details are given on the approach taken to conduct the study.
- ii) Life Cycle Inventory (LCI), where the product system and its constituent unit processes are described, and exchanges between the product system and the environment are compiled and evaluated. These are called elementary flows; include inputs from nature (e.g. extracted raw materials, land used, raw materials and so on) and outputs to nature (e.g. emissions to air, water, and soil). The amounts of elementary flows exchanged by the product system and the environment are about one functional unit, as defined in the Goal and Scope phase.
- iii) Life Cycle Impact Assessment (LCIA), where the magnitude and significance of environmental impacts associated with the elementary flows compiled. This is done by associating the life cycle inventory results with environmental impact categories and category indicators. LCI results, other than elementary flows, are identified and their relationship to corresponding category indicators is determined. LCIA has several mandatory elements: selection of impact categories, category indicators, and characterization models as well as assignment of the LCI results to the various impact categories (classification) and calculation of category indicator results (characterization).

iv) Life Cycle Interpretation, where the findings of the previous two phases are combined with the defined goal and scope in order to reach conclusions or recommendations. It is important to note that Environmental-LCA provides an assessment of potential impacts based on a chosen functional unit

## 3.2. Goal and scope

The goal of this study was to evaluate the impact of Camelina, Safflower, Crambe and Flax derived HR-Jet Fuel on Green House Gases (GHG) emissions considering Global Warming Potential as comparative indicator, considering oilto-fuel system; following the RED (DIRECTIVE 2009/28/CE) recommendations, in that the requirements are:

- Carbon Dioxide (CO<sub>2</sub>); The effects were expressed as CO<sub>2</sub> equivalent using the following coefficients: CO<sub>2</sub>=1
- ii) methane (CH<sub>4</sub>); The effects were expressed as CO<sub>2</sub> equivalent using the following coefficients: CO<sub>2</sub>=23; and
- iii) nitrous oxide (N<sub>2</sub>O). The effects were expressed as CO<sub>2</sub> equivalent using the following coefficients: CO<sub>2</sub>=296.

The scope of this study holds the entire life cycle from cultivation until transport and distribution (to gate). The functional unit to witch the system impacts referred was the energy unit contained in HR Biojet fuel (one GJ of Biojet Fuel). The values of conversion factors were taken from and JEC E3 database as suggested by European harmonized calculation biofuel (BioGrace, 2016). N<sub>2</sub>O emissions were calculated following IPCC tier 1 (IPCC, 2006) as described below. For cultivation and oil extraction phases the impacts were evaluated by measured experimental data. On the other hand, to evaluate impacts due to oil to HR Biojet Fuel transformation phase a model for jet fuel production described by Li, X., & Mupondwa, E. (2014) were assumed. Standard data from RED was assumed in order to evaluate transport and distribution. In the system explation alternative uses of byproducts were considered when it was possible.

## 3.3. Life cycle inventory (LCI) modelling for agriproducts

For operations, we must take in count:

Production and maintenance of farm machinery, It is commonly suggested in agricultural LCA that the production of machinery and other capital equipment should be included in the inventory because they can have a relevant share of the overall impacts.(Acero, Rodríguez, & Ciroth, 2014) According to the project, scoping, site-specific data have been collected from farms in the selected place, while more generic data have been used for upstream production of farm inputs and downstream activities. Site-specific data on machinery use (use per year, expected lifetime, weight, etc.) have been collected from the studied farms in order to allocate the impacts of machinery production to the studied crops (Cardone et al., 2003; Gallejones et al., 2015; Lapola et al., 2010). The method selected is generally followed in the ecoinvent<sup>1</sup> database using software tools as openLCA or SimaPro to process information, where it has been implemented with a more sophisticated model (specific study of machinery production related emissions; detailed materials composition and so on). The assumptions and data conversions for the different life cycle stages of machinery considered in this study are explained in the following sections;

Manufacture Energy consumption and materials composition are representative of different agricultural machines, and have therefore been used as they appear in ecoinvent (Emissions from manufacture are included in ecoinvent). However, the reference flow for machinery datasets is a kg of machine, and this has been changed to hours or hectares to reflect the data collected in the inventory. When

<sup>&</sup>lt;sup>1</sup> For further information, please visit: http://www.ecoinvent.org/database/database.html.

doing so, site-specific data on machinery weight, lifespan and yearly usage have been used to parameterize the ecoinvent data in the following way where the first element represents the flows recorded in the ecoinvent datasets (Canals, Muñoz, McLaren, & Miguel, 2007; Dreyer et al., 2010). The allocation to the total units (hours or hectares) used in the machine's lifetime is done in the ecoinvent datasets for field work processes, and thus needs to be removed from there once it has been done in the machine's manufacture.

Maintenance and repairs the considerations done in ecoinvent for maintenance (change of tires, mineral oil, filters, batteries, etc.) are considered valid for this project. In the case of repairs, an increase of the manufacture materials is considered depending on the machine type (Nemecek, Frick, Dubois, & Gaillard, 2001; Spugnoli & Dainelli, 2013) . For tillage machines this is considered to be 45% extra material (steel); as specific data on this materials is easily collected in the farms (representing the frequency of change of tillage components such as harrow tines), this will be used instead(Enrique, Rodríguez, Ii, Raúl, & Serrano, 2014; Van Der Werf, 2004). Therefore, the steel input in the ecoinvent datasets for tillage machines is reduced by 45% and then increased by the calculated site-specific amount. The data collected from farmers actually shows quite dramatic increases in steel consumption when calculated like this, with e.g. increases of 200-264% (instead of the suggested 45%) for repairs in ploughs and power harrows.

Land use associated to farm buildings Nemecek et al. (2004) offer data on space requirements for different machines. It has been assumed that a shed is available in all farms to shelter all machines, and that a space equivalent to the requirement of each machine is provided all year-long. Therefore, the data in m2 offered by ecoinvent are directly converted to m2/year for each machine. The m2/year are then allocated to the functional output of the machine for one year. Area occupied by farm sheds is classified as 'Occupation, urban, discontinuously built' in ecoinvent. A similar approach has been used for the other buildings in the farm used for the studied vegetables. The area used by these buildings has been

obtained from the farmers and classified as 'Occupation, urban, discontinuously built'. Specific data for land use by farm buildings are provided in LCA reports for the different farms studied.

Use of agricultural machinery (field works) Fuel consumption for the different operations has been assessed specifically for the studied farms. This figure has then substituted the figures reported in ecoinvent, plus all subsequent emissions related to fuel consumption. The same sources used in ecoinvent for fuel emissions in agricultural machinery have been used, specifically for CO, HC (expressed as NMVOC) and NOx (Nemecek et al. 2004, Table A10), which differ substantially respect road vehicles. The emissions of CO, HC, NOx are expressed in g/h (Nemecek et al. 2004, Table A10), depending on each different operation; these emissions are re-calculated with the duration of the operations obtained from the farmers using the parameter rate\_h (dividing the duration in hours/ha obtained from the farmers by the duration expressed in ecoinvent (Nemecek et al. 2004, Table A9). To update fuel-related emissions (CO2, SO2, Pb, methane... Nemecek et al. 2004, table 7.1) the parameter rate fuel (fuel consumption per ha in RELU divided by fuel consumption per hectare in ecoinvent) is created and used for multiplying inputs (fuel consumption) and outputs related to fuel (most air emissions).

Completely representative: duration of operation lies within ±20% of that reported in ecoinvent. Partly representative: duration of operation lies within ±21-50% of that reported in ecoinvent. Not representative: duration of operation over 50% Consideration of manual labor with very few exceptions (e.g. Piringer and Steinberg 2006; Nguyen and Gheewala in press) the environmental impacts associated with human labor have systematically been excluded from LCA studies. The reason most often argued for this is that labor-force maintenancerelated environmental impacts (e.g. food consumption by workers; energy use for shelter; etc.) would occur regardless of the studied system (Piringer and Steinberg 2006). I.e. that person would still eat (and possibly work elsewhere) if the studied system was not in place. Piringer and Steinberg (2006) assess the

energy costs of labor in wheat production in the USA, concluding that this is of minor importance. According to their findings, labor-related energy would represent maximum 7.1% of energy use for wheat if the highest estimate for labor energy use is compared to the best estimates (i.e. not highest values) for the other items of the energy bill. It should be noted that there is a huge uncertainty in this value. In any case, it could be argued that 'in terms of energy efficiency at least, it would be a little unfair to compare the energy balance of non-mechanized or partly mechanized systems with fully mechanized ones without accounting for human labor input's (Shabbir Gheewala, 19.06.2007 e-mail communication in LCA forum). In this study, we have considered that impacts of maintaining humans are not affected by the studied system (i.e. food consumption, housing, etc. are excluded from the study), but that work-related transportation is increased by the studied system. Hence, an estimation of labor related transport has been done for labor-intensive operations. The nature of labor force in agricultural sector varies widely between the assessed countries, and so the way in which these impacts have been assessed also varies. In any case, the attempts done in this study have to be seen only as a first try to assess the relevance of labor transport-related impacts, and not as an exhaustive absolute statement of environmental impacts related to agricultural human labor in different countries.

Labor-intensive operations First, a focus has been placed on those operations that the farmers consider as 'labor intensive'. These are generally all operations that cannot be mechanized, such as harvesting of lettuces, brassica or green beans; hand weeding within rows; installation/removal of irrigation infrastructure; etc. In the UK and Spain most of these operations coincide (with a trend in Spain to perform more operations manually), whereas in Uganda the assessed farms show a much lower degree of mechanization, with use of tractors and machinery being the exception rather than the rule. However, in Uganda most farm workers travel to the field by bike or on foot, and so their transportation impacts have been neglected. The labor-intensive operations recorded for the LCA studies do not match the labor costs that could be found in the farm accounting books. As a rule of thumb, all permanent workers would be omitted from the LCA study, because they generally perform operations with high energy use (e.g. mechanized farm

operations, where the tractor fuel use will override the fuel use of their private cars) or with low labor input per unit of product (e.g. in a packing plant). On the other hand, it is usually the temporary workers who perform the labor-intensive operations. This study has tried to provide a first estimate of the importance of transportation of temporary workers for some of the studied crops.

Moreover, it is fundamental to determine an allocation factor formula in order to reassign impact to the mainstream (functional unit) and downstream (byproducts) present in agricultural processes (D'Avino et al., 2015; Spugnoli et al., 2012) it was used when system expansion was no possible.

Energy approach is one of the best for this dissertation, considering the type of product (bio fuel):

 $Allocation \ Factor = \frac{Output \ x \ Output \ LHV}{(Output \ x \ Output \ LHV) + (byproducts \ x \ byproducts \ LHV)} (1)$ 

This allocation formula explains how the energy content or lower heating value (LHV) is used for the redistribution of the impacts in; yield of the crop and its straw or epigeous residues or in further process along the productive chain allocation along the productive chain was performed according to (D'Avino et al., 2015).

Figure 10. System boundaries for a cradle-to-farm-gate Life Cycle Assessment (LCA) agricultural productions. The figure represents a simplified scheme of all the variables considered in the LCA calculations of agricultural productions.(J. H. Schmidt, 2008)



## 3.4. Emissions to air in farming phase

Regarding methane, it is not considering following recommendation of FAO and other institutions, in agriculture only selected crops has to estimate methane emission to air.

N<sub>2</sub>O emissions estimation, emissions of N<sub>2</sub>O from the agricultural phase were estimated according to the methodology developed by the Intergovernmental Panel on Climate Change (IPCC, 2006c) guidelines, chapter 11. Were consider direct and indirect annual N<sub>2</sub>O emissions from agricultural residuals and fertilizers that are calculated using:

- i) direct N<sub>2</sub>O emitted from fertilizer applied, using equation (2);
- ii) indirect N<sub>2</sub>O emitted from fertilizer applied, using equation (3);
- iii) direct N<sub>2</sub>O emitted from agricultural residues, using equation (4);
- iv) indirect N<sub>2</sub>O emitted from agricultural residues, using equation (5).

Were, the direct emission is a function of N inputs (Fsn and Fon that means Applied synthetic fertilizer Applied organic fertilizer respectively), emission factor for direct emission (EF1) and the  $N_2O$  / N molar relation (1.5714). There is no irrigation and tillage consider. this study ignores animal excretion and consider that methane was no produced.

(2)

$$Indirect \ N_2O(Fert) = ([(Fsn + Fon) * EF5 * FrLeac] + [Fsn * EF4 * FrGas]) * 1.5714$$
(3)

Were, the indirect emission is a function of N inputs (Fsn and Fon that means Applied synthetic fertilizer and Applied organic fertilizer respectively); emission factor for N2O emissions from atmospheric deposition of N on soils and water surface (EF4); emission factor for N<sub>2</sub>O emissions from N leaching and runoff (EF5); fraction of synthetic fertilizer N that volatilizes as NH<sub>3</sub> and NOx, kg N volatilized (FrGas); fraction of all N added to/mineralized that is lost through leaching and runoff (FrLeac); in and the N<sub>2</sub>O / N molar relation (1.5714).

$$Direct N_2O(residuals) = (Bgr * Nbg) * EF1 * 1.5714$$
(4)

Were, the direct and indirect emission is a function of below ground residues (Bgr) and its N content (Nbg)

$$Indirect \ N_2O(Fert) = (Bgr * Nbg) * EF5 * FrLeac * 1.5714$$
(5)

#### 3.5. Bio-based product systems description and analysis

Considering all possibilities in figure 12, a few were considered in the systems under study as show below:



3.5.1. Camelina crop

Camelina can be grown in a variety of land types, at low fertilizer application and lower maintenance costs, and has been grown with virtually no herbicides or pesticides (Li & Mupondwa, 2014) and extra irrigation was no required. The seeding rates, yield, and fertilizer application rate used in this study are average data from experimental units located in Bologna and Pisa- Italy, along three years (2013-2015) shown in Table 6. Emission to air were assumed that only N<sub>2</sub>O and CO<sub>2</sub> were produced along farming phase. In the case of emissions to water, Nitrogenous, Phosphorous and its consequent chemical oxygen demand were no considered. Emissions of N<sub>2</sub>O from the agricultural phase were estimated according to the methodology developed by the Intergovernmental Panel on Climate Change (IPCC) guidelines, chapter 11, using formulas 2,3,4,5.

Considering Camelina by products, two of them were considered:

- Camelina derived cake, according to several studies it's useful to be blended into animal and fish feed (Frame et al., 2007; Gibbons & Hughes, 2011; Peiretti & Meineri, 2007), indeed, FDA has approved the use of camelina meal in animal and fish until of 10% w/w. in this particular case, camelina meal has been used to evaluate its impact replacing fish meal into trout feed (10%);
- ii) Camelina straw, it can be used potentially for animal bedding or making fiber products (Li & Mupondwa, 2014), similar to flax straw. However, an industrial application is not known in Italy, consequently this study ignores alternative products from camelina straw, that can be considered zero emission waste.

## 3.5.2. Flax crop

Flax can be grown in a variety of land types, at low fertilizer application and lower maintenance costs, and has been grown with virtually no herbicides or pesticides and extra irrigation was no required. The seeding rates, yield, and fertilizer application rate used in this study are average data from three years (2013-2015) surveys carried out in Bologna and Pisa- Italy, shown in Table 7. Emission to air were assumed that only N<sub>2</sub>O and CO<sub>2</sub> were produced along farming phase following FAO recommendations. In the case of emissions to water, Nitrogenous, Phosphorous and its consequent chemical oxygen demand were considered.

Emissions of N<sub>2</sub>O from the agricultural phase were estimated according to the methodology developed by the Intergovernmental Panel on Climate Change (IPCC) guidelines, chapter 11, described in point 3.4. Flax straw can be used potentially for animal bedding or making fiber products, for paper, bio-building and so on (Kissinger et al., 2007; Yan et al., 2014). Actually, an industrial application in Italy was to use flax straw into paper pulp mill. On the other hand,

flax cake was no considered as by products instead it was considered as zero residues waste.

#### 3.5.3. Crambe crop

Crambe can be grown in a variety of land types, at low fertilizer application and lower maintenance costs, and has been grown with virtually no herbicides or pesticides and extra irrigation was no required. The seeding rates, yield, and fertilizer application rate used in this study are average data from experimental units located in Bologna and Pisa- Italy, along three years (2013-2015) shown in Table 8. Emission to air were assumed that only N<sub>2</sub>O and CO<sub>2</sub> were produced along farming phase. In the case of emissions to water, Nitrogenous, Phosphorous and its consequent chemical oxygen demand were no considered. Emissions of N<sub>2</sub>O from the agricultural phase were estimated according to the methodology developed by the Intergovernmental Panel on Climate Change (IPCC) guidelines, chapter 11, using formulas 2,3,4,5. Considering Crambe by products, there was no considered any of them, them were no usable at this moment in industrial applications.

#### 3.5.4. Cartamo crop

Cartamo can be grown in a variety of land types, at low fertilizer application and lower maintenance costs, and has been grown with virtually no herbicides or pesticides and extra irrigation was no required. The seeding rates, yield, and fertilizer application rate used in this study are average data from experimental units located in Bologna and Pisa- Italy, along three years (2013-2015) shown in Table 9. Emission to air were assumed that only N<sub>2</sub>O and CO<sub>2</sub> were produced along farming phase. In the case of emissions to water, Nitrogenous, Phosphorous and its consequent chemical oxygen demand were no considered. Emissions of N<sub>2</sub>O from the agricultural phase were estimated according to the methodology developed by the Intergovernmental Panel on Climate Change (IPCC) guidelines, chapter 11, using formulas 2,3,4,5 in point 3.4.

Considering Cartamo by products, two of them were considered:

- i) Cartamo derived cake, according to several studies it's useful to be blended into animal and fish feed (Frame et al., 2007; Gibbons & Hughes, 2011; Peiretti & Meineri, 2007), this cake is very like camelina's one. Indeed, considering that FDA has approved the use of camelina meal in animal and fish until of 10% w/w. in this particular case, camelina meal has been used to evaluated its impact replacing fish meal into trout feed (10%) and several studies Cartamo cake can be used until 10% w/w (Clementi et al., 2014; Ragni et al., 2015);
- ii) Cartamo straw, it can be used potentially for animal bedding or making fiber products (Li & Mupondwa, 2014), similar to flax straw. However, an industrial application is not known in Italy, consequently this study ignores alternative products from camelina straw, that can be considered zero emission waste.

#### 3.5.5. Oil extraction

Oil extraction was performed by a pressing plant (double extraction), with a nominal power of 18 kW, a working time of 900 h year <sup>-1</sup> and a capacity of 160 kg of seeds h<sup>-1</sup>. The residual oil content in the press cake was around 10%, confirming that around of 90% of the total oil content had been extracted. Electricity consumption for seed crushing and defatting was 0.324 MJ kg<sup>-1</sup> of seed and considering a CO<sub>2</sub> release of 129.19 g CO<sub>2</sub>eq MJ<sup>-1</sup>for electricity production at low voltage (JEC E3 database). The choice of applying the mechanical pressing extraction process (instead of solvent-defatting process) achieved a defatted seed meal with a higher nutritional value due to the residual oil content that is used to replace fish meal, allowing a system expiation in order to perform a more accurate evaluation (D'Avino et al., 2015).

### 3.5.6. Transformation of oils (Jet Fuel)

There are two common alternative fuel technologies for producing two types of jet fuels: Fischer–Tropsch (FT) fuels to replace conventional kerosene fuels and hydro-processed renewable jet (HRJ) fuels made from hydro-processed oils. Camelina, Cartamo Flax and Crambe are good sources for alterative jet fuels that has drawn attention from commercial ventures and airlines (Moser, 2010). The first step in the oil-to-HRJ conversion is the removal of oxygen via decarboxylation and hydrodeoxygenation mechanisms (Kalnes et al., 2010). Hydrogen is a required reagent in the decarboxylation pathway. Subsequently, selective cracking and isomerization are required to reduce the carbon number into the jet range and achieve key jet fuel properties such as freeze and flash points (IATA, 2010).

There are also many catalytic options to control the isomerization and hydrocracking steps. The primary inputs into the HRJ production process are similar to a typical refining system, and include steam, natural gas, cooling water, and electrical power. To determine the range of mass and energy input of camelina derived HRJ, two scenarios were commonly used from literature (EPA, 2013; Stratton, 2010) which were both modified based on soybean oil processing. Water and natural gas assumptions were adapted from an industrial scale-up by Miller and Kumar (2013). In this case, scenario I was assumed in order to assess non-food crops oils sustainability.

Figure 12. Data input for camelina derived HR Jet fuel, sources: (Li & Mupondwa, 2014; Miller & Kumar, 2013)

Jet fuel production	Scenario I	Scenario II
Inputs		
Oil	46.3995 g	41.5788 g
Hydrogen	0.2892 g	1.4040 g
Electricity	$2.0187 \times 10^{-3}$ kWh	$2.2386 \times 10^{-3} \text{ kWh}$
Natural gas	0.3237 MJ	0.3237 MJ
NaOH		0.0572 g
Phosphoric acid		0.0331 g
Water	$2.1091 \times 10^{-3} \text{ m}^3$	$2.1091 \times 10^{-3} \text{ m}^3$
Transportation by truck	4.5375 kg km	4.5375 kg km
Outputs		
HRJ fuel	1 MJ	1 MJ
Avoid product — naphtha	3.4890 g	10.8918 g
Avoid product – LPG	2.5429 g	1.9946 g
Avoid product — propane	1.7897 g	
Avoid product – diesel	9.8614 g	
Heat, waste	$7.2673  imes 10^{-3} \text{ MJ}$	$8.0590 \times 10^{-3} \text{ MJ}$

### 3.6. Data Analysis

To evaluate the similarities within results, two types of test were performed:

- Student's t test for compared means between tested sites and reported comparison data. This test (as described below) assumes: A normal (gaussian) distribution for the populations of the random errors, and there is no significant difference between the standard deviations of both population samples.
- Metric Multidimensional Scaling (MDS), this clustering test makes similarities measurements based on the distance within the given variables, to make clear the crops and sites similarities in terms of their yield, NER, land use, oil content and GWP.
# **CHAPTER 4**

#### 4. Results.

#### 4.1. LCA on Camelina

Global Warming Potential along the productive chain of Camelina was mostly influenced by farming phase. In figure 13 it is observable mean values of GWP and energy requirement of Camelina until oil extraction in the system frontiers, using energy based allocation (considering mass and energy flows).

Table 6. Characterization of the agricultural phase input and outputs related to a hectare of Camelina. Reporting mean and relative standard deviation of three years data. (DM dry matter; N nitrogenous content).

Inputs and outputs	Unit	Bolo	ogna	Pisa		
Farming inputs		Mean	RSD (%)	Mean	RSD (%)	
Seeds	kg/ha	12,50	0,00	12,50	0,00	
Organic N (Urea)	kg/ha	16,00	43,31	0,00	0,00	
Inorganic N (Anhydrous ammonia)	kg/ha	22,33	41,16	66,00	34,00	
P <sub>2</sub> O <sub>5</sub>	kg/ha	0,00	0,00	76,33	8,00	
K <sub>2</sub> O	kg/ha	0,00	0,00	53,33	87,00	
Pesticide	kg/ha	0,00	0,00	0,07	0,00	
Diesel	kg/ha	167,00	0,00	118,67	13,00	
Farming outputs		Mean	RSD (%)	Mean	RSD (%)	
Seed yield	kg/ha	533,33	31,20	833,33	8,00	
Above ground residues	kg/ha	2727,40	34,51	1667,67	9,00	
Below ground residues	kg/ha	513,76	39,20	394,84	26,00	
DM seed oil	%	39,37	2,41	35,09	16,00	
Seed LHV	MJ/kg	23,93	1,22	21,70	5,00	
DM Below ground residues N	%	1,12	18,75	0,55	18,00	

In Table 6, it is shown the comparative requirements of the tested sites along three years (2013-2015). The most important things to point out, regarding farming phase inputs and outputs were:

- i) the lower yield in Bologna, it was around 36% compared with Pisa one;
- ii) the diesel consumption in Bologna that was 29% higher than Pisa; and
- iii) Fertilizer used in Bologna that were lower than Pisa in every trial.

Furthermore, Pisa has required phosphates and potassium fertilizer that do not contribute to N<sub>2</sub>O production, however, they contribute to GWP and energy requirement as well as nitrogenized ones.

At the agricultural stage, it is noticeable that GWP per hectare, considering only inputs, present no difference in mean values. On the other hand, the variability among data is greater in Bologna due to organic and inorganic N-fertilizers used, and the variability observed in Pisa is mainly influenced by potassium fertilized applied, diesel consumption and inorganic N-fertilizers used. (As shown in tables 7 and 8).

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	BOLOGNA	Input	Process energy (Mjfossil/ha)	GWP (kg CO2eq/ha)	Input	Energy (Mjfossil/ha)	GWP (kg CO2eq/ha)	Input	Process energy (Mjfossil/ha)	GWP (kg CO2eq/ha)	Energy (Mjfossil/ha)	GWP (kg CO2eq/ha)
Seeds	К В	12,50	98,38	5,00	12,50	98,38	5,00	12,50	98,38	5,00	98,38	5,00
Phytosanitary	Pesticide (kg)	0,00	0,00	0,00	00'0	0,00	0,00	0,00	00'0	0,00	0,00	0,00
Fuels	Diesel (L)	167,00	8349,33	630,76	167,00	8349,33	630,76	167,00	8349,33	630,76	8349,33	630,76
zers	P <sub>2</sub> O5 (kg)	00'0	00'0	0,00	00'0	00'0	0,00	0,00	0,00	0,00	00'0	00'0
ic Fertili	K <sub>2</sub> O (kg)	00'0	0,00	00'0	0,00	0,00	0,00	0,00	0,00	00'0	0,00	00'0
Inorgan	lnorganic N (Anhydrous ) (kg)	27,00	1198,53	79,00	00'0	0,00	0,00	40,00	1775,60	117,04	991,38	65,35
Organic Fertilizers	Organic N (Urea) (kg)	12,00	432,00	37,82	12,00	432,00	37,82	24,00	864,00	75,65	576,00	50,43
	Others	00'0	0,00	00'0	0,00	0,00	0,00	00'0	0,00	0,00	0,00	0,00
Total			10078,24	752,59		8879,71	673,58		11087,31	828,45	10015,08	751,54

Table 7. Camelina GHG (kg of  $CO_2eq$ ) for input in farming phase (Bologna)

		<b>ر</b>	0 1	ŝ	2	0 7 9	4	ſ	104	ю	Σu	a a
	PISA	Input	Energy (Mjfossil/ha)	GWP (kg CO2eq/ha)	Input	Process energy (Mjfossil/ha)	GWP (kg CO2eq/ha)	Input	Process energy (Mjfossil/ha)	GWP (kg CO2eq/ha)	Energy (Mjfossil/ha)	GWP (kg CO2eq/ha)
Seeds	ß	12,50	98,38	5,00	12,50	98,38	5,00	12,50	98,38	5,00	98,38	5,00
Phytosanitary	Pesticide (kg)	0,00	0,00	00'0	0,10	0,10	0,00	0,10	0,10	0,00	0,07	00'0
Fuels	Diesel (L)	101,00	5049,60	381,48	130,00	6499,48	491,01	125,00	6249,50	472,13	5932,86	448,20
ſS	P <sub>2</sub> O <sub>5</sub> (kg)	69,00	1050,87	69,74	80,00	1218,40	80,86	80,00	1218,40	80,86	1162,56	77,15
nic Fertilize	K <sub>2</sub> O (kg)	0,00	00'0	0,00	80,00	774,40	46,09	80,00	774,40	46,09	516,27	30,73
Inorgar	Inorganic N (Anhydrous) (kg)	40,00	1775,60	117,04	79,00	3506,81	231,15	79,00	3506,81	231,15	2929,74	193,12
Organic Fertilizers	Organic N (Urea) (kg)	0,00	0)00	00'0	00′0	0,00	0,00	00′0	0,00	0,00	00'0	00′0
	Others	0,00	0,00	00′0	00'0	0,00	0,00	00'0	0,00	0,00	00′0	00'0
Total			7974,44	573,26		12097,57	854,11		11847,59	835,22	10639,86	754,20

Table 8. Camelina GHG (kg of  $CO_2eq$ ) for input in farming phase (Pisa)

Considering total GWP associated to a hectare (inputs and emissions to air), the most influencing input was Diesel in Bologna and Pisa, however in Bologna its influence is 1,6 folds higher than Pisa; the second factor to take in count is GWP due to N<sub>2</sub>O emission to air that is higher in Pisa (100 kgCO<sub>2</sub>eq/ha more than Bologna). Concluding that Pisa has produced 11% more GHG emission per hectare than Bologna in farming phase.

Figure 13. Camelina system considering oil as mainstream product and meal and straw as byproducts.



In this analysis, N<sub>2</sub>O emission to air were calculated in base of N-fertilizers and below ground residues (N-content) in farming stage (according to formulas 2-5). These results have shown that Camelina grown in Pisa produces almost 36% more emission of N<sub>2</sub>O to air (1,68 kg/ha) than Bologna (figure 14). The variability or increasing of N<sub>2</sub>O emission is principally due to the difference on N-fertilizers applied (66 kg/ha in Pisa and 38,2 kg/ha in Bologna, no differencing whether it was organic or inorganic ones) despising whether it was direct or indirect emitted as presented in figure 14. On the other hand, below ground residues has demonstrated no greater influence on results. Thus, variability is directly influenced by the same factors pointed out before.

Figure 14.  $N_2O$  emission from fertilizers use and below ground residues of Camelina.



Considering that LCA results are discussed based on GWP. It was computed in term of grams of  $CO_2$  as the equivalent substance released into atmosphere (only N<sub>2</sub>O and CO<sub>2</sub> in this case, for emission to air produced by farming phase). It is

noticeably that the diesel contribution is particularly high in Bologna (Figure.15), influencing negatively its GHG emissions. However, referring GHG to a hectare the results are similar between tested sites, counting the different factor influencing results. On the contrary, referring to the yield (grains), there were great differences, and Bologna had the lower yield between the compared sites (see table 6) influencing negatively GWP results along the chain. It has been observed that N-fertilizers use is one of the most important factor influencing agricultural LCA results. Regarding that, N-fertilizer use in Bologna (closer to 38 kg/ha), is noticeably lower than in Pisa. However, diesel influence over GHG is greater than N-fertilizer in Bologna as showed in Figure 16.

Figure 15. Relative Global Warming Potential referred to a kilogram of grain produced (Camelina).



In the extraction phase, the oil and meal production were mainly influenced by oil content and extraction efficiency that increase the variability saw in farming phase, considering that oil content in Bologna (39,4%) was high that Pisa (35,09%) as shown in table 6. Contrastingly, oil produced in bologna was lower

due to it low yield. As consequence, electricity needed to extract oil in Pisa was higher (14%) due to a lower oil content raising its GWP as shown in table 9.



Figure 16. Emission for a kilogram of grain (Camelina)

Considering the GWP of oil and meal production, before allocation, in mean Bologna impact was lower that Pisa (15%). Moreover, GWP is directly influenced by farming phase that represent over 95% of impact of oil and meal in both sites, as shown in table 10. On the other hand, referring GWP to functional unit it is noticeable that Pisa reduces its impact due to a greater production compared to Bologna as shown in table 11.

Table 9. Extraction production of oil and meal and electricity consumption of Camelina.

Extrac pha	ction ise	Grain (kg)	Oil (%)	Oil output (kg)	Oil output (MJ)	Meal output (kg)	Meal output (MJ)	Electricity (MJ) / oil (kg)	Oil (kg)/Seed (kg)
	2013	590,00	40,30%	214,70	8373,30	375,30	8980,93	0,89	0,36
LOGNA	2014	500,00	39,40%	181,63	7083,73	318,37	7618,50	0,89	0,36
BO	2015	538,89	38,43%	193,46	7544,78	345,43	8266,21	0,90	0,36
	2013	760,00	39,80%	277,05	10805,01	482,95	11556,96	0,89	0,36
PISA	2014	810,00	36,49%	279,45	10898,55	530,55	12696,06	0,94	0,35
	2015	870,00	28,98%	229,20	8938,98	640,80	15334,23	1,23	0,26

Table 10. Total GWP of Camelina Oil until extraction phase.

GWP		GWP grain	WP grain GWP heat GWP		Total (kg CO₂eq)
	2013	1041,55	3,42	24,70	1069,67
BOLOGNA	2014	773,15	2,89	20,93	796,97
	2015	1228,82	3,08	22,56	1254,46
	2013	829,71	4,41	31,81	865,93
PISA	2014	1349,79	4,45	33,91	1388,15
	2015	1336,76	3,65	36,42	1376,83

After performing an energy based allocation (see equation 1), GHG emission from Camelina derived bio-jet fuel were 95,76  $gCO_{2eq}/MJ$  in Pisa and 130,02  $gCO_{2eq}/MJ$  in Bologna. Taking as reference value of 83,8  $gCO_{2eq}/MJ$  of biofuel

recommend by RED, there was no reduction. On the other hand, comparing results with conventional Jet Fuel reported by Lokesh et. Al., there was a reduction of around 9% was observed in Pisa and an increase of 22% was observed in Bologna.

Moreover, considering system expansion (camelina meal replacing fish meal in fish feed production (1:1) until 10% w/w), GHG emission from Camelina jet fuel were 76.29 gCO<sub>2eq</sub>/MJ in Pisa and 110,01 gCO<sub>2</sub>eq/MJ in Bologna, regarding that fish meal has an impact 1,16 times high that Camelina meal regarding GWP. Taking as reference value of 83,8 gCO<sub>2eq</sub>/MJ of biofuel recommend by RED, there was a considerable reduction only at Pisa (around 20%). While comparing results with conventional Jet Fuel reported by Lokesh, there was a reduction of 38% was observed in Pisa and a minimal increase was observed in Bologna compared with fossil origin jet fuel. System expansion is described in figures 17-18.

	Bologn	a	Pisa		
Energy based Allocation					
	Not allocated	Allocated	Not allocated	Allocated	
Farming	214,62	102,41	180,34	68,53	
Oil extraction	5,44	2,61	5,88	2,23	
Jet Fuel production	24,00	24,00	33,00	24,00	
Transport	1.00	1.00	1.00	1.00	
Transport	1,00	1,00	1,00	1,00	
	245.00	120.02	217 22	05.70	
i otai (gCO <sub>2</sub> / MJ)	245,06	130,02	217,22	95,76	

#### Table 11. Allocated GWP of Camelina derived HR Jet Fuel

Figure 17. System expansion of Camelina derived jet fuel in Bologna based on the functional unit.



Figure 18. System expansion of Camelina derived jet fuel in Pisa based on the functional unit.



Expanding system, using Camelina meal as replace for fishmeal, it has reduced impact in both sites. However, reduction in Bologna is not enough to arrive to fossil Jet Fuel. In Pisa, a greater reduction has been performed replacing Camelina meal, reducing emission until 76,29 gCO<sub>2</sub>/MJ that is lower than fossil Jet Fuel and Biofuel reference value 83gCO<sub>2</sub>/MJ (RED). It is important to point out that system expansion has increase the environmental performance in both cases, furthermore, Pisa Jet Fuel has potential to reduce GWP in aircrafts (almost 30 gCO<sub>2</sub>eq/MJ) as shown in figure 19.

Figure 19. System expansion results and comparison with several references (Lokesh et al., 2015; Peng et al., 2015, RED).



According to Lokesh and coworkers (2015) GHG emitted by Camelina Jet fuel production were 101 gCO<sub>2eq</sub>/MJ, our results have presented a considerable reduced GHG emission in Pisa using allocation and system expansion methods. The worst scenery (Bologna) has presented no reduction compared with fossil jet fuel nor camelina derived jet fuel produced in Canada. Regarding the Net Energy

Ratio (NER), Lokesh and coworker (2015) reported 1,16 MJ Fossil/ MJ of Jet Fuel and Li, X., & Mupondwa, E. (2014) reported 1,25 MJ Fossil/ MJ of Jet Fuel. In our results Pisa NER is closer to these results (1,29 MJ Fossil/ MJ of Jet Fuel), whereas, in Bologna it was considerable higher (2,13 MJ Fossil/ MJ of Jet Fuel) in concordance with GWP results. All results including energy balance and GHG emission were strongly influenced by Agricultural stage and its variable inputs requirement for GWP and NER.

## 4.2. LCA on Flax

Global Warming Potential along the productive chain of Flax is mostly influenced by farming phase. In figure 20 it is observable mean values of GWP and energy requirement of Flax until oil extraction under the system frontiers, then using energy based allocation (mass and energy flow were considered) to reduce mainstream GWP.

Table 12. Characterization of the agricultural phase input and outputs related to a hectare of Flax. Reporting mean and relative standard deviation of three years data. (DM dry matter; N nitrogenous content).

Inputs and outputs	Unit	Bolo	ogna	Pisa		
Farming inputs		Mean	RSD (%)	Mean	RSD (%)	
Seeds	kg/ha	30,00	0,00	39,22	3,00	
Organic N (Urea)	kg/ha	16,00	43,31	0,00	0,00	
Inorganic N (Anhydrous ammonia)	kg/ha	22,33	41,20	82,66	9,77	
P <sub>2</sub> O <sub>5</sub>	kg/ha	0,00	0,00	53,33	86,66	
K <sub>2</sub> O	kg/ha	0,00	0,00	53,33	87,00	
Pesticide	kg/ha	0,00	91,00	0,67	86,66	
Diesel	kg/ha	167,00	0,00	118,67	16,54	
Farming outputs		Mean	RSD (%)	Mean	RSD (%)	
Seed yield	kg/ha	1633,33	39,83	1566,67	7,30	
Above ground residues	kg/ha	6233,46	22,80	3891,03	5,08	
Below ground residues	kg/ha	813,04	25,00	381,65	25,00	
DM seed oil	%	44,40	1,62	45,67	1,22	
Seed LHV	MJ/kg	25,11	1,01	22,24	5,00	
DM Below ground residues N	%	0,81	15,07	0,40	37,68	

In Table 12, it has been shown the comparative requirements of the tested sites along three years (2013-2015). The most important things to point out, regarding farming phase inputs were:

- the yield in Bologna and Pisa were very close, however in Bologna it was around 4% higher that Pisa one;
- ii) the diesel consumption in Bologna that was 29% higher than Pisa;
- iii) Fertilizer used in Bologna were lower (only N-fertilizers were applied); and;
- iv) In Pisa, few pesticides were used contrastingly with Bologna.

Considering farming outputs, there is a big difference that influence GWP: adobe ground residues in Bologna is considerable higher (almost 100% higher than Pisa) as presented in table 7. Furthermore, Pisa has required phosphates and potassium fertilizers, that do not contribute to N<sub>2</sub>O production, however, they contribute to GWP as well as nitrogenated ones, considering their production.

At the agricultural stage, these are the inputs to be under control in order to reduce GHG emissions in tested zones. Furthermore, it is noticeable that GWP per hectare, considering only inputs, present no difference in mean values. On the other hand, the variability among data is greater in Bologna due to organic and inorganic N-fertilizers used, and the variability observed in Pisa is mainly influenced by potassium fertilized applied, diesel consumption and inorganic N-fertilizers used (as shown in table 13-14).

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BOLOGNA		Input	Process energy (Mjfossil/ha)	GWP (kg CO2eq/ha)	Input	Process energy (Mjfossil/ha)	GWP (kg CO2eq/ha)	Input	Process energy (Mjfossil/ha)	GWP (kg CO2eq/ha)	Energy (Mjfossil/ha)	GWP (kg CO2eq/ha)
Seeds	kg	30'00	236,10	12,60	30'00	236,10	12,60	30'00	236,10	12,60	236,10	12,60
Phytosanitary	Pesticide (kg)	00'0	00′0	00′0	00'0	00′0	0,71	00'0	00′0	00′0	00′0	0,24
Fuels	Diesel (L)	167,00	8350,00	631,26	167,00	8350,00	631,26	167,00	8350,00	631,26	8350,00	631,26
ې ۲	P <sub>2</sub> O <sub>5</sub> (kg)	0),00	00'0	0,00	0),00	00'0	0,00	0),00	00′0	00'0	0,00	0,00
: Fertilize	K <sub>2</sub> O (kg)	00'0	0,00	0,00	00'0	0,00	00'0	00'0	0,00	00'0	00'0	0,00
Inorganic	Inorganic N (Anhydrous)	27,00	1198,53	79,11	00'0	0,00	0,00	40,00	1775,60	117,20	991,38	65,44
Organic Fertilizers	Organic N (Urea) (kg)	12,00	432,00	37,80	12,00	3220,80	37,80	24,00	864,00	37,80	1505,60	37,80
	Others		0),00	0,00		0),00	0,00		0),00	00'0	00'0	00'0
Total			10216,63	760,77		11806,90	682,37		11225,70	798,86	11083,08	747,33

Table 13. Flax GHG (kg of CO2eq) for input in farming phase (Bologn
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PISA		Input	Energy (Mjfossil/ha)	GWP (kg CO2eq/ha)	Input	Energy (Mjfossil/ha)	GWP (kg CO2eq/ha)	Input	Energy (Mjfossil/ha)	GWP (kg CO2eq/ha)	Energy (Mjfossil/ha)	GWP (kg CO2eq/ha)
Seeds	kg	38,00	299,06	15,96	40,00	314,80	16,80	40,00	314,80	16,80	309,55	16,52
Phytosanitary	Pesticide (kg)	00'0	00'0	00′0	1,00	286,40	10,97	1,00	286,40	10,97	190,93	7,31
Fuels	Diesel (L)	96,00	4800,00	362,88	130,00	6500,00	491,40	130,00	6500,00	491,40	5933,33	448,56
5	P <sub>2</sub> O <sub>5</sub> (kg)	0,00	00'0	00'0	80,00	1218,40	80,80	80,00	1218,40	80,80	812,27	53,87
nic Fertilize	K <sub>2</sub> O (kg)	0,00	0,00	0,00	80,00	774,40	46,40	80,00	774,40	46,40	516,27	30,93
Inorga	Inorganic N (Anhydrous)	92,00	4083,88	269,56	78,00	3462,42	228,54	78,00	3462,42	228,54	3669,57	242,21
Organic Fertilizers	Organic N (Urea) (kg)	00'0	0,00	0),00	00'0	0,00	0),00	00'0	0,00	0,00	0),00	0),00
	Others	00'0	0,00	0,00	00'0	0,00	0,00	00'0	0,00	0,00	0,00	0,00
Total			9182,94	648,40		12556,42	874,91		12556,42	874,91	11431,93	799,41

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Considering total GWP associated to a hectare (inputs and emissions to air), the most influencing input was Diesel in Bologna and in Pisa was N<sub>2</sub>O emission, however in Bologna the influence of diesel was around 1.6 folds higher than Pisa and the second factor to take in count is GWP due to N<sub>2</sub>O emission in Bologna. N<sub>2</sub>O emission was evident higher in Pisa (263,21 kgCO<sub>2</sub>eq/ha more than Bologna). Concluding that Pisa has produced 24% more GHG emission per hectare than Bologna.





In this analysis, N<sub>2</sub>O emission to air were calculated in base of N-fertilizers and below ground residues (% N-content) in farming stage (according to formulas 2-5). These results have shown that Flax crop in Pisa produces around 50% more emission of N<sub>2</sub>O (1,771 kg/ha) than Bologna (0,894 kg/ha) as shown in figure 14. The variability or increasing of N<sub>2</sub>O emission is principally due to the difference on N-fertilizers applied (82,66 kg in Pisa and 38,20 in Bologna, considering whether it was organic or inorganic ones) despising whether it was direct or indirect emitted as presented in figure 21. On the other hand, below ground residues has demonstrated no greater influence on results. Thus, variability is directly influenced by the same factors pointed out in farming phase.



Figure 21. N<sub>2</sub>O emission from fertilizers use and below ground residues of Flax.

Considering that GHG emission results are discussed based on GWP and it was computed in term of grams of CO<sub>2</sub> as the equivalent substance released into atmosphere (only N<sub>2</sub>O and CO<sub>2</sub> in this case, for emission to air produced by farming phase). It is noticeably that the diesel contribution is particularly high in Bologna (Figure 22), influencing negatively its GHG emissions. However, referring GHG to a hectare the results are similar between tested sites, counting the different factor influencing results. On the contrary, referring to the yield, there

are great differences, and Bologna had the greater yield between the compared sites (see table 12), rather it is close to yield in Pisa. It has been observed that N-fertilizers use is one of the most important factor influencing agricultural LCA results. Regarding that, N-fertilizer use in Bologna (closer to 38 kg/ha), is noticeably lower than in Pisa (82,66 kg/ha). However, diesel influence over GHG is greater than N-fertilizer in Bologna as showed in figure 22 and figure 23.

Figure 22. Relative Global Warming Potential referred to a kilogram of grain produced (Flax).



In the extraction phase, the oil and meal production are mainly influenced by oil content and agro-production of seeds that increase the variability saw in farming phase considering that oil content in Bologna (44,40%) was lower than Pisa (45,67%) as shown in table 6. Contrastingly, oil produced in Bologna was lower due to it low yield, however, there was merely difference with Pisa. As consequence, electricity needed to extract oil in Pisa was higher (2,20%) due to a lower oil content raising its GWP as shown in table 15.



Figure 23. Emission for a kilogram of grain of Flax (considering only extraction phase).

When the GWP of a hectare is referred to yield (figure 23), the influence of inputs and N<sub>2</sub>O emission (relative) has no changed compared with figure 22 (data not

shown). On the other hand, the GWP of a kilogram in clearly higher in Pisa (12,50%) as the results of GWP per hectare, this is due to GHG from N<sub>2</sub>O and inorganic N-fertilizers, in this case, yield and oil content have no greater influence over results in figure 23. The difference was over that 12,50% affecting negatively to environmental performance of Camelina grown in Pisa, however the performance of Flax in Pisa is also great compared with other crops in study.

Extr pl	action hase	Grain (kg)	Oil content (%)	Oil output (kg)	Oil output (MJ)	Meal output (kg)	Meal output (MJ)	Electricity (MJ) / oil (kg)	Oil (kg)/Seed (kg) Heat (MJ) /oil (kg)
A	2013	1000,000	43,7%	417,069	16265,708	582,931	13949,529	0,777	0,417 0,065
NDO-	2014	2300,000	45,8%	978,968	38179,768	1321,032	31612,286	0,761	0,426 0,064
BOI	2015	1600,000	43,8%	645,356	25168,881	954,644	22844,633	0,803	0,403 0,068
	2013	1500,000	46,4%	631,995	24647,805	868,005	20771,360	0,769	0,421 0,065
ISA	2014	1700,000	45,4%	753,360	29381,040	946,640	22653,095	0,731	0,443 0,061
	2015	1500,000	45,3%	615,624	24009,322	884,376	21163,126	0,789	0,410 0,066

Table 15. Extraction production of oil and meal and electricity and heat consumption for Flax chain.

Considering the GWP of oil and meal production inputs and outputs as shown in table 15, before allocation, in mean Bologna impact was lower that Pisa (around 15%). Moreover, GWP is directly influenced by farming phase that represent over 95% of impact of oil and meal in both sites, as shown in table 16.

Total GWP referred to 1 ha	GWP grain	GWP heat	GWP Electricity	Total (kgCO <sub>2 eq</sub> )

Table 16. Total GWP of Flax Oil until extraction phase (not allocated)

	2013	1041,55	3,42	24,70	1069,67
BOLOGNA	2014	773,15	2,89	20,93	796,97
	2015	1228,82	3,08	22,56	1254,46
	2013	829,71	4,41	31,81	865,93
PISA	2014	1349,79	4,45	33,91	1388,15
	2015	1336,76	3,65	36,42	1376,83

On the other hand, referring GWP to oil mass and oil energy content it is noticeable that Bologna reduces its impact due to a greater production compared to Pisa as shown in table 17.

Table 17. GWP of oil production referred to mass and energy output (not allocated)

Not allocated	I GWP	kg CO2/kg oil	gCO2/MJ oil
	2013	2,62	67,29
BOLOGNA	2014	0,97	24,79
BOLOGINA	2015	2,03	52,13
	Mean	1,87	48,07
	2013	2,13	54,65
DISA	2014	1,96	50,26
TISA	2015	2,38	61,00
	Mean	2,16	55,30

After performing an energy based allocation to jet fuel system (see equation 1), GHG emission from Camelina derived bio-jet fuel were 73,67 gCO<sub>2</sub>eq/MJ in Pisa and 62,60 gCO<sub>2</sub>eq/MJ in Bologna. Taking as reference value of 83,8 gCO<sub>2eq</sub>/MJ of biofuel recommend by RED, there was quite reduction in Pisa and a bit greater reduction in Bologna. On the other hand, comparing results with conventional Jet Fuel reported by Lokesh (106 gCO2eq/MJ), there was a considerable reduction of around 30% in Pisa and 41% in Bologna.

Figure 24. System expansion of Flax derived jet fuel in Bologna based on the functional unit.



Figure 25. System expansion of Flax derived jet fuel in Pisa based on the functional unit.



Expanding system, using Flax straw as replace for eucalyptus wood into paper pulp mill (figures 23-24), it has reduced impact in both sites. GWP is considerable lower in every scenario under system expansion. In the best case, Bio-jet fuel produced in Bologna had a GWP of -148,44 gCO<sub>2</sub>eq/MJ that means that Bio jet fuel produced in Bologna and using its by-product (straw) as feedstock to produce paper can reduces the GHG (assuming replace 1:1 into paper pulp mill). On the other hand, Jet Fuel produced in Pisa has a GWP of 81,77 gCO<sub>2</sub>eq/MJ.

	Bolog	na	Pisa		
Energy based Allocation	Not allocated	Allocated	Not allocated	Allocated	
Farming	61,84	33,18	81,11	44,31	
Oil extraction	6,47	3,47	6,25	3,41	
Jet Fuel production	24,95	24,95	24,95	24,95	
Transport	1,00	1,00	1,00	1,00	
Total (gCO <sub>2</sub> /MJ)	94,26	62,60	113,31	73,67	

#### Table 18. Allocated GWP of Flax derived HR Jet Fuel

Figure 26. System expansion of bio-jet fuel chain, results and comparison with several references of biofuels (Lokesh et al., 2015; Peng et al., 2015, RED).



It is important to point out that system expansion has increase the environmental performance in Bologna, it is due to a bigger straw production in this site that reduces the environmental impact of it (see table 12), furthermore, Pisa Jet Fuel has potential to reduce GWP in aircrafts (almost 25 gCO<sub>2</sub>eq/MJ). Moreover, Pisa performance was better considering an energy based allocation respect to the system expansion.

According to Lokesh and coworkers (2015) GHG emitted by Camelina Jet fuel production were 101 gCO<sub>2</sub>eq/MJ, our results have presented a considerable reduced GHG emission in Bologna and Pisa using allocation and system expansion methods. The worst scenery (Pisa), under energy based allocation, has presented a greater reduction compared with fossil jet fuel (30%) nor Camelina derived jet fuel produced in Canada (26,7%). In Bologna, system expansion has produced a net reduction of -148,4 gCO<sub>2</sub>eq/MJ that makes feasible to produce bio-jet fuel to save emission in airlines operation.

Regarding the Net Energy Ratio (NER), Lokesh and coworker (2015) reported 1,16 MJ Fossil/ MJ of Jet Fuel and Li, X., & Mupondwa, E. (2014) reported 1,25 MJ Fossil/ MJ of Jet fuel derived from Camelina oil. In our results Pisa NER is closer to these results (1,18 MJ Fossil/ MJ of Jet Fuel), whereas, in Bologna it was considerable lower (1,03 MJ Fossil/ MJ of Jet Fuel) in concordance with GWP results. All results including energy balance and GHG emission were strongly influenced by Agricultural stage and its variable inputs requirement for GWP and NER.

### 4.3. LCA on Crambe

Considering Crambe chain, it was mostly influenced by farming phase as pointed out before. In figure 27 it is observable mean values of GWP and energy invested to obtain oil and meal under the system frontiers, then using energy based allocation (mass and energy flow were considered) to reduce mainstream GWP.

Table 19. Characterization of the agricultural phase input and outputs related to a hectare of Crambe. Reporting mean and relative standard deviation of three years data. (DM dry matter; N nitrogenous content)

Inputs and outputs	Unit	Bolo	ogna	Pisa		
Farming inputs		Mean	RSD (%)	Mean	RSD (%)	
Seeds	kg/ha	12,50	0,00	12,50	0,00	
Organic N (Urea)	kg/ha	16,00	43,31	0,00	0,00	
Inorganic N (Anhydrous ammonia)	kg/ha	22,33	41,16	59,50	46,00	
$P_2O_5$	kg/ha	0,00	0,00	74,50	8,00	
K <sub>2</sub> O	kg/ha	0,00	0,00	40,33	87,00	
Pesticide	kg/ha	0,00	0,00	0,05	0,00	
Diesel	kg/ha	167,50	0,00	118,67	13,00	
Farming outputs		Mean	RSD (%)	Mean	RSD (%)	
Seed yield	kg/ha	1410,33	31,20	630,00	8,00	
Above ground residues	kg/ha	3200,40	38,51	1570,67	29,00	
Below ground residues	kg/ha	530,06	39,00	350,84	20,00	
DM seed oil	%	33,70	15,41	23,09	30,00	
Seed LHV	MJ/kg	22,83	1,22	22,70	5,00	
DM Below ground residues N	%	0,60	18,75	0,80	18,00	

In Table 19, it has been shown the comparative inputs of the tested sites along three years (2013-2015). The most important things to point out were:

- the yield in Bologna extremally higher than the yield in Pisa, at least 2,25 folds high;
- ii) the diesel consumption in Bologna that was 14% higher than Pisa;
- iii) Fertilizer used in Bologna were lower (only N-fertilizers were applied); and;
- iv) In Pisa, few pesticides were used contrastingly with Bologna, where there was almost no pesticide use.

Considering farming outputs, there was a big difference that influence GWP in every step: adobe ground residues in Bologna is considerable higher (almost 4,5 folds higher than Pisa) as presented in table 8. Furthermore, Pisa has required phosphates and potassium fertilizers, that did not contribute to N<sub>2</sub>O production, however, they have contributed to GWP as well as nitrogenized ones, considering their production.

At the agricultural stage diesel consumption and fertilizes use were the inputs to be under control to reduce GHG emissions in tested zones. Furthermore, it was noticeable that GWP per hectare, considering only inputs, present no difference in mean values. On the other hand, the variability among data was greater in Bologna due to organic and inorganic N-fertilizers used, and the variability observed in Pisa was mainly influenced by potassium fertilized applied, diesel consumption and inorganic N-fertilizers used (as shown in table 20-21).

Table 20. Crambe GHG (kg of  $CO_2eq$ ) for input in farming phase (Bologna).

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	Acid	Input	Process energy (MJ fossil/ha)	GWP (kg CO2eq/ha)	Input	Process energy (MJ fossil/ha)	GWP (kg CO2eq/ha)	Input	Process energy (MJ fossil/ha)	GWP (kg CO2eq/ha)	Process energy (MJ fossil/ha)	GWP (kg CO2eq/ha)
Seeds	kg	12,50	98,38	5,00	12,50	98,38	5,00	00'0	0,00	0,00	65,58	5,00
Phytosanitaries	Pesticide (kg)	00'0	0,00	0,00	0,10	28,64	0,00	00'0	0,00	0,00	9,55	0,00
Fuels	Diesel (L)	101,00	5050,00	381,78	130,00	6500,00	491,40	0,00	0,00	0,00	3850,00	436,59
s	P205 (kg)	69,00	1050, 87	69,69	80,00	1218, 40	80,80	0,00	0,00	0,00	756,4 2	75,25
Fertilizen	K2O (kg)	0,00	00′0	0,00	80,00	774,40	46,40	0,00	00′0	0,00	258,13	23,20
Inorganic	Inorganic N (Anhydrous)	40,00	1775,60	117,20	00'62	3506,81	231,47	00'0	0,00	0,00	1760,80	174,34
Organic Fertilizers	Organic N (Urea) (kg)	00'0	0,00	0,00	00'0	0,00	0,00	00'0	0,00	0,00	0,00	00'0
	Others	0,00	00'0	00'0	00′0	00'0	00'0	00′0	00'0	0,00	00'0	00'0
Total			7974,85	573,67		12126,63	855,07		0,00	0,00	6700,49	714,37

Table 21. Crambe GHG (kg of  $CO_2eq$ ) for input in farming phase (Pisa).

Considering total GWP associated to a hectare (inputs and emissions to air), the most influencing input was Diesel in Bologna and; in Pisa was N<sub>2</sub>O emission, however in Bologna the influence of diesel was around 1,6 folds higher than Pisa and the second factor to take in count is GWP due to N<sub>2</sub>O emission in Bologna. N<sub>2</sub>O emission was evident higher in Pisa (263,21 kgCO<sub>2</sub>eq/ha more than Bologna). Concluding that Pisa has produced 24% more GHG emission per hectare than Bologna.

Figure 27. Crambe system considering oil as mainstream product and meal and straw as byproducts.



In this analysis, N<sub>2</sub>O emission to air were calculated in base of N-fertilizers and below ground residues (% N-content) in farming stage (according to formulas 2-5). These results have shown that Flax crop in Pisa produces around 50% more emission of N<sub>2</sub>O (1,771 kg/ha) than Bologna (0,894 kg/ha) as shown in figure 14. The variability or increasing of N<sub>2</sub>O emission is principally due to the difference on N-fertilizers applied (82,66 kg in Pisa and 38,20 in Bologna, considering whether it was organic or inorganic ones) despising whether it was direct or indirect emitted as presented in figure 21. On the other hand, below ground residues has demonstrated no greater influence on results. Thus, variability is directly influenced by the same factors pointed out in farming phase.



Figure 28.  $N_2O$  emission from fertilizers use and below ground residues of Crambe.

Considering that GHG emission results are discussed based on GWP and it was computed in term of grams of  $CO_2$  as the equivalent substance released into atmosphere (only N<sub>2</sub>O and CO<sub>2</sub> in this case, for emission to air produced by farming phase). It is noticeably that the diesel contribution is particularly high in Bologna (Figure 22), influencing negatively its GHG emissions. However, referring GHG to a hectare the results are similar between tested sites, counting the different factor influencing results. On the contrary, referring to the yield, there

are great differences, and Bologna had the greater yield between the compared sites (see table 19), rather it is close to yield in Pisa. It has been observed that N-fertilizers use is one of the most important factor influencing agricultural LCA results. Regarding that, N-fertilizer use in Bologna (closer to 38 kg/ha), is noticeably lower than in Pisa (82.66 kg/ha). However, diesel influence over GHG is greater than N-fertilizer in Bologna as showed in figure 22 and figure 23.

Figure 29. Relative Global Warming Potential referred to a kilogram of grain produced (Flax).



In the extraction phase, the oil and meal production are mainly influenced by oil content and agro-production of seeds that increase the variability saw in farming phase considering that oil content in Bologna (44,40%) was lower than Pisa (45,67%) as shown in table 6. Contrastingly, oil produced in Bologna was lower due to it low yield, however, there was merely difference with Pisa. As consequence, electricity needed to extract oil in Pisa was higher (2,20%) due to a lower oil content raising its GWP as shown in table 22.



Figure 30. Emission for a kilogram of grain of Crambe (considering only extraction phase).

When the GWP of a hectare is referred to yield (figure 23), the influence of inputs and N<sub>2</sub>O emission (relative) has no changed compared with figure 22 (data not shown). On the other hand, the GWP of a kilogram in clearly higher in Pisa (12,50%) as the results of GWP per hectare, this is due to GHG from N<sub>2</sub>O and

inorganic N-fertilizers, in this case, yield and oil content have no greater influence over results in figure 23. The difference was over that 12,50% affecting negatively to environmental performance of Camelina grown in Pisa, however the performance of Flax in Pisa is also great compared with other crops in study.

Table 22. Extraction production of oil and meal and electricity and heat
consumption for Crambe chain.

Extractio	on phase	Grain (kg)	Oil content (%)	Oil output (kg)	Oil output (MJ)	Meal output (لام)	Meal output (MJ)	Electricity (MJ) / oil	(kg) Oil (kg)/Seed	Heat (MJ) / oil (kg)
4	2013	1625,16	34,10%	554,18	21613,04	1070,98	25628,60	0,95	0,34	0,08
LOGN	2014	1700,00	36,20%	615,40	24000,60	1084,60	25954,48	0,90	0,36	0,08
BOI	2015	903,46	30,70%	277,32	10815,45	626,14	14983,64	1,06	0,31	0,09
	2013	599,67	27,94%	167,55	6534,35	432,12	10340,66	1,16	0,28	0,10
PISA	2014	661,24	17,96%	122,64	4782,96	538,60	12888,77	1,75	0,19	0,15
	2015	0,00	0,00%	0,00	0,00	0,00	0,00	0,00	0,00	0,00

Table 23. Total GWP of Crambe Oil until extraction phase (not allocated).

Total GWP rej	ferred to 1 ha	GWP grain	GWP heat	GWP Electricity	Total (kg CO₂eq)
	2013	1011,30	30,48	68,03	1109,80
BOLOGNA	2014	762,47	33,85	71,16	867,48
	2015	1221,98	15,25	37,82	1275,05
	2013	837,35	9,22	25,10	871,67
PISA	2014	1361,31	6,75	27,68	1395,73
	2015	0,00	0,00	0,00	0,00
Considering the GWP of oil and meal production inputs and outputs as shown in table 17, before allocation, in mean Bologna impact was lower that Pisa (around 15%). Moreover, GWP is directly influenced by farming phase that represent over 95% of impact of oil and meal in both sites, as shown in table 23.

On the other hand, referring GWP to oil mass and oil energy content it is noticeable that Bologna reduces its impact due to a greater production compared to Pisa as shown in table 24.

Not alloc	ated GWP	kg CO2/kg oil	gCO2/MJ oil
	2013	2,00	51,35
ROLOCNA	2014	1,41	36,14
BOLOGNA	2015	4,60	117,89
	Mean	2,67	68,46
2013		5,20	133,40
DICA	2014	5,20	291,81
PISA	2015	0,00	0,00
	Mean	5,20	212,61

Table 24. GWP of oil production referred to mass and energy output (not allocated).

After performing an energy based allocation to jet fuel system (see equation 1), GHG emission from Crambe derived bio-jet fuel were 64,99 gCO<sub>2</sub>eq/MJ in Bologna and 129,40 gCO<sub>2</sub>eq/MJ in Pisa. Taking as reference value of 83,8 gCO<sub>2</sub>eq/MJ of biofuel recommend by RED, there was quite reduction in Bologna and a bit greater increment in Bologna. On the other hand, comparing results with conventional Jet Fuel reported by Lokesh (106 gCO<sub>2</sub>eq/MJ), there was a considerable reduction of around 40% in Pisa.

	Bolo	gna	Pis	a
Energy based Allocation	Not allocated	Allocated	Not allocated	Allocated
Farming	86,11	38,96	315,04	103,65
Oil extraction	2,29	1,03	2,29	0,75
Jet Fuel production	25,00	24,00	25,00	24,00
Transport	1,00	1,00	1,00	1,00
Total (gCO <sub>2</sub> /MJ)	114,40	64,99	343,33	129,40

Regarding the Net Energy Ratio (NER), Lokesh and coworker (2015) reported 1,16 MJ Fossil/ MJ of bio-jet fuel and Li, X., & Mupondwa, E. (2014) reported 1,25 MJ Fossil/ MJ of Jet fuel produced from Camelina oil. In our results, bio-jet fuel derived from Crambe oil has shown; in Bologna NER was closer to these results (1,18 MJ Fossil/ MJ of Jet Fuel), whereas, in Pisa it was considerable higher (1,53 MJ Fossil/ MJ of Jet Fuel) in concordance with GWP results. All results including energy balance and GHG emission were strongly influenced by Agricultural stage and its variable inputs requirement for GWP and NER.

## 4.4. LCA on Cartamo

The environmental performance of Cartamo chain is mostly influenced by farming phase as the other crops in study. In figure 31 it is observable mean values of GWP and energy invested to obtain oil and meal under the system frontiers, then using energy based allocation (mass and energy flow were considered) to reduce mainstream GWP.

Table 26. Characterization of the agricultural phase input and outputs related to a hectare of Cartamo. Reporting mean and relative standard deviation of three years data. (DM dry matter; N nitrogenous content)

Inputs and outputs	Unit	Bolo	ogna	Р	isa
Farming inputs		Mean	RSD (%)	Mean	RSD (%)
Seeds	kg/ha	28,33	10,00	22,00	16,00
Organic N (Urea)	kg/ha	16,00	43,31	0,00	0,00
Inorganic N (Anhydrous ammonia)	kg/ha	22,33	41,20	84,00	34,00
P <sub>2</sub> O <sub>5</sub>	kg/ha	0,00	0,00	76,33	8,00
K <sub>2</sub> O	kg/ha	0,00	0,00	53,33	87,00
Pesticide	kg/ha	0,39	91,00	2,53	100,00
Diesel	kg/ha	159,30	0,00	137,33	15,00
Farming outputs		Mean	RSD (%)	Mean	RSD (%)
Seed yield	kg/ha	2213,50	55,70	980,68	35,63
Above ground residues	kg/ha	16138,28	4,00	3557,49	63,60
Below ground residues	kg/ha	1500,00	15,00	549,64	80,00
DM seed oil	%	20,30	11,00	21,10	5,50
Seed LHV	MJ/kg	20,77	1,22	22,24	5,00
DM Below ground residues N	%	0,52	18,75	0,55	46,88

In Table 26, it has shown the comparative inputs of the tested sites along three years (2013-2015). The most important things to point out, regarding farming phase inputs were:

- v) the yield in Bologna extremely higher than the yield in Pisa, at least 2,25 folds high;
- vi) the diesel consumption in Bologna that was 14% higher than Pisa;
- vii) Fertilizer used in Bologna were lower (only N-fertilizers were applied); and;
- viii) In Pisa, few pesticides were used contrastingly with Bologna, where there was almost no pesticide use.

Considering farming outputs, there is a big difference that influence GWP: adobe ground residues in Bologna is considerable higher (almost 4,5 folds higher than Pisa) as presented in table 9. Furthermore, Pisa has required phosphates and potassium fertilizers, that do not contribute to N<sub>2</sub>O production, however, they contribute to GWP as well as nitrogenized ones, considering their production.

At the agricultural stage, these are the inputs to be under control to reduce GHG emissions in tested zones. Furthermore, it is noticeable that GWP per hectare, considering only inputs, present no difference in mean values. On the other hand, the variability among data is greater in Bologna due to organic and inorganic N-fertilizers used, and the variability observed in Pisa is mainly influenced by potassium fertilized applied, diesel consumption and inorganic N-fertilizers used (as shown in table 27-28).

		ſ	101	3	ſ	107	4	ſ	101	ъ	Β	<b>م</b> 2
	BULUGNA	Input	Process energy (Mjfossil/ha)	GWP (kg CO <sub>2</sub> eq/ha)	Input	Process energy (Mjfossil/ha)	GWP (kg CO <sub>2</sub> eq/ha)	Input	Process energy (Mjfossil/ha)	GWP (kg CO <sub>2</sub> eq/ha)	Energy (Mjfossil/ha)	GWP (kg CO <sub>2</sub> eq/ha)
Seeds	Kg	30,00	236,10	12,60	30,00	236,10	12,60	25,00	196,75	10,50	222,98	11,90
Phytosanitaries	Pesticide (kg)	0,07	17,45	0,71	0,07	17,45	0,71	1,03	275,11	11,24	103,33	4,22
Fuels	Diesel (L)	159,30	7965,00	602,15	159,30	7965,00	602,15	159,30	7965,00	602,15	7965,00	602,15
sı	P <sub>2</sub> O <sub>5</sub> (kg)	0,00	00'0	0,00	0,00	00'0	0,00	0,00	00'0	0,00	00'0	0,00
nic Fertilize	K <sub>2</sub> O (kg)	00′0	00'0	00'0	00′0	00'0	00'0	00′0	00'0	00′0	00′0	00′0
Inorgar	Inorganic N (kg)	27,00	1198,53	79,11	00'0	00'0	0,00	40,00	1775,60	117,20	991,38	65,44
Organic Fertilizers	Organic N (Urea) (kg)	12,00	432,00	37,80	12,00	3220,80	37,80	24,00	864,00	37,80	1505,60	37,80
	Others	00′0	0),00	0,00	00'0	0,00	0,00	00'0	0),00	0,00	00'0	0,00
Total			9849,08	732,38		11439,35	653,27		11076,46	778,90	10788,29	721,51

Table 27. Cartamo GHG (kg of  $CO_2eq$ ) for input in farming phase (Bologna).

Total		Organic	Inorgan	nic Fertilizers		Fuels	Phytosanitaries	Seeds		
		Fertilizers							PISA	
	Others	Organic N	Inorganic N	K <sub>2</sub> O (kg)	P <sub>2</sub> O <sub>5</sub> (kg)	Diesel (L)	Pesticide (kg)	kg		
		(Urea)	(ammonia) (kg)							
	00'0	0,00	00'26	00'0	69,00	116,00	0,01	26,00	Input	
11365,33	0,00	0,00	4305,83	00'0	1050,87	5800,00	4,01	204,62	Energy	201
803,45	0,00	00'0	284,21	0,00	69,69	438,48	0,15	10,92	(Mjfossil/ha) GWP (kg	13
							200		CO <sub>2</sub> eq/ha)	
12773.24	0.00	0.00	3462.42	au,uu 774.40	o0,00 1218.40	00.000 6900.00	260.62	20,000 157.40	niput Process energy	2
895,76	0,00	00′0	228,54	46,40	80,80	521,64	9,98	8,40	(Mjfossil/ha) GWP (kg	014
									CO <sub>2</sub> eq/ha)	
	00'0	0,00	78,00	80,00	80,00	158,00	6,66	20,00	Input	
15420,04	0,00	0,00	3462,42	774,40	1218,40	7900,00	1907,42	157,40	Process energy	201
1034,44	00'0	0,00	228,54	46,40	80,80	597,24	73,06	8,40	(Mjfossil/ha) GWP (kg	15
13186,21	00'0	0,00	3743,56	516,27	1162,56	6866,67	724,02	173,14	CU <sub>2</sub> eq/na) Energy	
									(Mjfossil/ha)	Me
911,22	00'0	0),00	247,10	30,93	77,10	519,12	27,73	9,24	GWP (kg	ean
									CO <sub>2</sub> eq/ha)	

Table 28.	Cartamo GHG	(kg of CO <sub>2</sub> eq)	) for input in	farming phase	(Pisa).
			,	01	· /

Considering total GWP associated to a hectare (inputs and N<sub>2</sub>O), the most influencing input is Diesel in Bologna and Pisa, however in Bologna its influence is 1.6 folds higher than Pisa and the second factor to take in count is GWP due to N<sub>2</sub>O emission that is higher in Pisa (almost 298 kgCO<sub>2</sub>eq/ha more than Bologna). Concluding that Pisa has produced 33,30% more GHG emission per hectare than Bologna, affecting the chain along.





In this analysis, N<sub>2</sub>O emission to air were calculated in base of N-fertilizers and below ground residues (% N-content) in farming stage (according to formulas 2-5). These results have shown that Cartamo grown in Pisa produces almost 2 times more emission of N<sub>2</sub>O (1,907 kg/ha) than Bologna (figure 28). The variability or increasing of N<sub>2</sub>O emission is principally due to the difference on N-fertilizers applied (84 kg/ha in Pisa and 38,22 kg/ha in Bologna, considering whether it was organic or inorganic ones) despising whether it was direct or indirect emitted as presented in figure 31. On the other hand, below ground residues has demonstrated no greater influence on results. Thus, variability is directly influenced by the same factors pointed out before.



Figure 32.  $N_2O$  emission from fertilizers use and below ground residues of Cartamo.

Considering that GHG emission results are discussed based on GWP and it was computed in term of grams of CO<sub>2</sub> as the equivalent substance released into atmosphere (only N<sub>2</sub>O and CO<sub>2</sub> in this case, for emission to air produced by farming phase, using equivalence coefficients cited in methodology). It is noticeably that the diesel contribution to GWP is particularly high in Bologna (Figure 32). In other word 62% of GHG emitted by farming phase were due to diesel used in there, influencing negatively the total of GHG emissions in Bologna. However, referring GHG to a hectare the results are similar between tested sites, counting the different factor influencing results. On the contrary, referring to the yield, there are great differences, and Bologna had the greater

yield between the compared sites (see table 9). It has been observed that N-fertilizers use is one of the most important factor influencing agricultural LCA results. Regarding that, N-fertilizer use in Bologna (closer to 38 kg/ha), is noticeably lower than in Pisa (82,66 kg/ha). However, diesel influence over GHG is greater than N-fertilizer in Bologna as showed in figure 31 and figure 32. Contrasting with the other crops under study, Cartamo in Pisa has required four times more phytosanitary compared with Camelina, Flax and Crambe.





In the extraction phase, the oil and meal production were mainly influenced by oil content and agro-production of seeds that increase the variability saw in farming

phase considering that oil content in Bologna (20,35%) was lower than Pisa (21,11%) as shown in table 6. Contrastingly, oil produced in Bologna was greater due to it higher yield (see table 28). As consequence, electricity requirement to extract oil in Pisa was lower (5,20%) due to a lower oil content raising Bologna oil's GWP as shown in table 29.



Figure 34. Emission for a kilogram of grain of Cartamo (considering only farming phase).

When the GWP of a hectare is referred to yield (figure 34), the influence of inputs and N<sub>2</sub>O emission (relative) has no changed compared with figure 33 (data not shown). On the other hand, the GWP of a kilogram of grain in clearly higher in Pisa (58,30%) as the results of GWP per hectare, this is due to GHG from N<sub>2</sub>O and inorganic N-fertilizers, in this case, yield and oil content have the greater influence over results variability in figure 34. The difference was over that 50% affecting negatively to environmental performance of Camelina grown in Pisa.

Table 29. Extraction production of oil and meal and electricity and heat consumption for Cartamo chain.

E	xtraction phase	Grain (kg)	Oil content (%)	Oil output (kg)	Oil output (INJ)	Meal output (kg)	Meal output (MJ)	Electricity (MJ) / oil (kg)	Oil (kg)/Seed (kg)	Heat (MJ) /oil (kg)
Ą	2013	1100,46	22,60%	248,70	9699,47	851,76	20382,55	1,43	0,23	0,12
00	2014	2000,00	20,40%	408,00	15912,00	1592,00	38096,56	1,59	0,20	0,13
BOL	2015	3540,05	18,05%	638,83	24914,25	2901,22	69426,25	1,80	0,18	0,15
	2013	1001,00	22,30%	223,22	8705,68	777,78	18612,17	1,45	0,22	0,12
PISA	2014	1319,56	20,44%	276,90	10799,10	1042,66	24950,82	1,54	0,21	0,13
-	2015	621,48	20,56%	127,78	4983,26	493,70	11814,29	1,58	0,21	0,13

Considering the GWP of oil and meal production inputs and outputs as shown in table 30, before allocation, in mean Bologna impact was lower than Pisa (around 28,02%) as shown in table 31. Moreover, GWP is directly influenced by farming phase that represent over 96% of impact of oil and meal in both sites, as shown in table 30.

Table 30. Total GWP of Cartamo Oil until extraction	phase	(not allocated)
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Not Allocated a hecta	(referred to are)	GWP grain	GWP heat	GWP Electricity	Total (kg CO₂eq/ha)
	2013	1001,35	13,68	46,06	1061,09
BOLOGNA	2014	743,87	22,44	83,72	850,02
	2015	1170,72	35,14	148,18	1354,04
	2013	1440,55	12,28	41,90	1494,73
PISA	2014	1395,22	15,23	55,23	1465,69
	2015	1542,74	7,03	26,01	1575,78

On the other hand, referring GWP to oil mass and oil energy content it is noticeable that Bologna reduces its impact due to a greater production compared

to Pisa as shown in table 31 and the difference observable is greater than the observed in table 30.

Not allo	cated GWP	kg CO₂/kg oil	gCO2/MJ oil
	2013	4,27	109,40
POLOCNA	2014	2,08	53,42
BOLOGNA	2015	2,12	54,35
	Mean	2,82	72,39
	2013	6,70	171,70
DICA	2014	5,29	135,72
FIJA	2015	12,33	316,21
	Mean	8,11	207,88

Table 31. GWP of oil production referred to mass and energy output (not allocated).

After performing an energy based allocation to jet fuel system (see equation 1), GHG emission from Cartamo derived bio-jet fuel were 73,67 gCO<sub>2</sub>eq/MJ in Pisa and 62,60 gCO<sub>2</sub>eq/MJ in Bologna. Taking as reference value of 83,8 gCO<sub>2eq</sub>/MJ of biofuel recommend by RED, there was quite reduction in Pisa and a bit greater reduction in Bologna. On the other hand, comparing results with conventional Jet Fuel reported by Lokesh (106 gCO<sub>2</sub>eq/MJ), there was a considerable reduction of around 30% in Pisa and 41% in Bologna as shown in table 27.

Figure 35. System expansion of Flax derived jet fuel in Bologna based on the functional unit.



Figure 36. System expansion of Flax derived jet fuel in Pisa based on the functional unit.



Expanding system, using Cartamo meal as replace for rapeseed/fish meal into trout feed system (figures 35-36), it has reduced impact only in Bologna comparing it with the GWP of fossil jet fuel (106 gCO<sub>2</sub>eq/MJ). GWP in Bologna was considerable lower in mean under system expansion (Figure 31). In the best case, Bio-jet fuel produced in Bologna had a GWP of -193,78 gCO<sub>2</sub>eq/MJ that means that Bio jet fuel produced in Bologna and using its by-product (meal) as feedstock to produce trout feed can reduces the GHG (assuming replace 1:1 until 10% w/w as Camelina meal). On the other hand, Jet Fuel produced in Pisa has a GWP of 208,22 gCO<sub>2</sub>eq/MJ, this was one of the worst performance in this study compared with Camelina, Falx and Crambe.

	Bolo	gna	Pis	а	
Energy based Allocation	Not allocated	Allocated	Not allocated	Allocated	
Farming	93,61	28,08	289,95	86,98	
Oil extraction	2,29	0,69	2,29	0,69	
Jet Fuel production	25,00	25,00	24,00	24,00	
Transport	1,00	1,00	1,00	1,00	
Total (gCO <sub>2</sub> /MJ)	121,90	54,77	317,24	112,67	

### Table 32. Allocated GWP of Cartamo derived HR Jet Fuel

It is important to point out that system expansion has increase the environmental performance in Bologna, it is due to a bigger straw production in this site that reduces the environmental impact of it (see table 26), furthermore, Pisa Jet Fuel has no potential to reduce GWP in aircrafts. Moreover, Pisa performance was better considering an energy based allocation respect to the system expansion as presented in figures 35-36 and table 32.

Figure 37. System expansion of bio-jet fuel chain, results and comparison with several references of biofuels (Lokesh et al., 2015; Peng et al., 2015, RED)



According to Lokesh and coworkers (2015) GHG emitted by Camelina Jet fuel production were 101 gCO<sub>2</sub>eq/MJ, additionally, for Cartamo Bio-Jet fuel produced in United States it was reported an GWP of 81 gCO<sub>2</sub>eq/MJ (Stratton, 2010) considering allocation method to estimate it. Accordingly, our results have presented a considerable reduced GHG emission in Bologna (33% compared to Stratton 2010) and greater compared to fossil jet fuel using allocation method and system expansion method has shown that Bologna bio-jet fuel produces a reduction of -193,78 gCO<sub>2</sub>eq/MJ. The worst scenery (Pisa), under energy based allocation, has presented a greater reduction compared with system expansion. On the other hand, the allocation method and system expansion has shown no reduction compared with fossil jet fuel.

Regarding the Net Energy Ratio (NER), Lokesh and coworker (2015) reported 1,16 MJ Fossil/ MJ of Jet Fuel and Li, X., & Mupondwa, E. (2014) reported 1,25 MJ Fossil/ MJ of Jet fuel derived from Camelina oil. In our results Pisa NER was higher than these results (1,76 MJ Fossil/ MJ of Jet Fuel), whereas, in Bologna it was considerable lower (1,01 MJ Fossil/ MJ of Jet Fuel) in concordance with GWP results. All results including energy balance and GHG emission were strongly influenced by Agricultural stage and its variable inputs requirement for GWP and NER.

### 4.5. Data analysis results

The statistical analysis has shown no difference in mean comparing Flax derived jet fuel GWP (energy based allocation) produced in Bologna and Pisa (p < 0,05). On the other hand, Camelina, Cartamo and Crambe has shown differences in average values (p > 0,05). Moreover, Camelina was the only with lower GWP in Pisa contrastingly with the other three crops tendency (see figure 38-39).



Figure 38. Statistical comparison on GWP (allocated), mean and typical error.

Analysis similarities and dissimilarities throughout MDS in figure 40, additionally the stress of the classification model (goodness of fit for MDS) was 0,9998 for the first coordinate and 0,9905 for the second concluding that had a good fit to data used. It was evident two main groups one integrated by Camelina, Cartamo and Crambe in Pisa (yellow ellipse), as shown in Figure 38 those were non-well performed crops. On the other hand, the best performance was attributable to Flax and Cartamo in Bologna and Flax in Pisa (red ellipse). Nevertheless, out grouping in Bologna we had Cartamo and in Pisa Camelina.



Figure 39. GWP consolidated by experimental location (mean and SD).

Figure 40. Multidimensional scaling clustering; legend Bologna (BO), Pisa (PI), Cartamo (Car), Camelina (Cam), Crambe (Cra) and Flax (Fla).



Considering land use, it was evident that Flax has the best performance, besides Cartamo in all crops. It had a great correlation with yield and oil content (%) as well as GWP, showing the same tendency. Table 33. Land use for all crops.

Land Use									
		Bologna		Pisa					
		Mean	SD	Mean	SD				
Camelina		2120.00	180.62	1560.00	168.79				
Cartamo	m <sup>2</sup> /GJ of Jet fuel	960.00	436.03	1980.00	714.58				
Crambe		650.00	242.78	1750.00	383.08				
Lino		620.00	257.49	620.00	69.94				

In term of energy investment and returned in the process, it was evident that flax has the best ratio, it has seemed to be related to inputs and energy required by the processes. The tendency was the same all around the study (see table 34).

Table 34. Net energy ratio resumes for all crops.

Net energy ratio								
		Bologna		Pisa				
		Mean	SD	Mean	SD			
Camelina	GJ fossil/ GJ produced	2.130	0.481	1.290	0.326			
Cartamo		1.010	0.607	1.760	0.363			
Crambe		1.180	0.272	1.580	0.523			
Lino		1.030	0.211	1.180	0.061			

# CHAPTER 5

### 5. Discussion

Farming outputs were very similar within the tested sites, only Cartamo crop has required pesticides in Pisa, differencing it from the other ones. On the other hand, inputs in Bologna were uniform considering that a great variability in yield. Furthermore, N<sub>2</sub>O emission produced in the farming phase were lower in any case in Bologna. Several studies (Gallejones et al., 2015; Lokesh et al., 2015; Miller & Kumar, 2013) have reported N<sub>2</sub>O for Camelina, Sunflower and other crops that are closer to our results; in Flax and Camelina in Pisa; and Flax and Cartamo in Bologna. In a study conducted in The Mediterranean zone (Bacenetti, Restuccia, Schillaci, & Failla, 2017), Flax has produced 1316 gCO<sub>2</sub>eq/kilogram of seed and Camelina has produced 1701 gCO<sub>2</sub>eq/kilogram of seed. In our results:

- i) Flax in Bologna has produced 710 gCO<sub>2</sub>eq/kilogram of seed; it represents 46% less emission compared with.
- ii) Flax in Pisa has emitted 819 gCO<sub>2</sub>eq/kilogram of seed; this assessment represents a reduction of 38% gCO<sub>2</sub>eq/kilogram of seeds.
- iii) Camelina in Bologna has shaped an GWP of 1913 gCO<sub>2</sub>eq/kilogram of seed; it shows GWP raising in almost 11%.
- iv) Camelina in Pisa has produced 1465 gCO<sub>2</sub>eq/kilogram of seed; this represents a reduction of 14%.

Considering these results, Flax has shown the greatest environmental performance within crops evaluated reducing considerably GWP compared with the same crop in a zone like the tested ones. Moreover, Cartamo assessment has demonstrated a reduction of GWP compared with Camelia and Flax in Bacenetti and coworkers research.

Another point to consider within this analysis is land use or m<sup>2</sup> of soil used to produce one functional unit, in this case food crops compete with non-food crops in order to use soil bringing problem to food supplies chain (Rebitzer et al., 2004; T. Schmidt, Fernando, Monti, & Rettenmaier, 2015). Indirect land use chance can be considering (land use changing from food to nonfood crops), in this regard the best performance is attributable to the crop which use less land to produce one functional unit (Bacenetti et al., 2017; Paper, 2002; Pawelzik et al., 2013). Actually, Flax has required less land to produce one GJ of bio-jet fuel considering the entire experiment. Furthermore, in Pisa Cartamo has required less land but it was under 10% lower than Flax (see table 33).

Considering the bio-jet fuel chain, oil content was, before yield, the most influencing factor in GWP along productive chain. In several studies (Bacenetti et al., 2017; Carlsson, 2009; Li & Mupondwa, 2014; Mihaela et al., 2013), the oil content has shown high variability, e.g. Flax and camelina seeds oil content ranges 25-50%. In our study, flax oil content has ranged 40-47% despising tested zone, as consequence Flax has represented the best oil yield in Bologna and Pisa. On the other hand, Cartamo seeds has presented a range of oil content of 18-24% indicative of the worst performance in terms of oil content. However, Cartamo seed yield in Bologna is one of the best in this study, making it up for a lower oil content.

GHG emitted by Camelina bio-jet fuel and biodiesel production, as reference crop, ranged 30-101 gCO<sub>2</sub>eq/MJ (Bacenetti et al., 2017; Li & Mupondwa, 2014; Lokesh et al., 2015). Camelina derived bio-jet fuel produced in Pisa was inside the range presented joined by Flax. On the other hand, in Bologna Flax and Cartamo derived jet fuel were within this range. It is remarkable that Flax derived jet fuel has represented the best crop considering the total assessment. Moreover, Cartamo in Bologna have presented a considerable reduced GHG emission Bologna. Regarding the Net Energy Ratio (NER), Lokesh and coworker (2015) reported 1,16 MJ Fossil/ MJ of Jet Fuel and Li, X., & Mupondwa, E. (2014) reported 1,25 MJ Fossil/ MJ of Jet Fuel. In our results Pisa NER is closer to these

results (1-1,87 MJ Fossil/ MJ of Jet Fuel), whereas, in Bologna it was considerable higher range (1-2,13 MJ Fossil/ MJ of Jet Fuel). All results including energy balance and GHG emission were strongly influenced by Agricultural stage and its variable inputs requirement followed by extraction phase.

Considering by product system expansion, Flax-straw pulp produced in Bologna has evidenced a reduction of almost three times the GWP with respect to eucalyptus (Hermann et al., 2007; Lopes et al., 2003), hemp (González-García et al., 2010) and Ecoinvent wood-pulp reference value. With respect to GWP impact of flax-straw pulp our results are similar to those evaluated in Canada (Kissinger et al., 2007) and Spain (S. González-García, Hospido, Feijoo, & Moreira, 2010), ranging 400-650 kgCO2eq/ton (data not shown). Pesticides use was zero for Bologna crop and minimal for Pisa crop (lower than 0,01 kg/ha), amount that is lower than the value reported in similar studies (González-García et al., 2009; Warrand et al., 2005). System expansion was the best option to reduce GHG. In the best case, it has produced a real reduction of 160 kgCO<sub>2</sub>eq /GJ of bio-jet fuel. In the system that consider Cartamo meal as a replaced of fish meal. On the other hand, Flax system expansion represent a reduction over 140 kgCO<sub>2</sub>eg /GJ of bio-jet fuel. Both due to their great byproduct yield (meal and straw). Camelina and Cartamo meal produced in Bologna has evidenced a reduction of almost 1,5 times the GWP with respect to fishmeal overseas (Avadí et al., 2015), and Ecoinvent fishmeal reference value. This has used to reduce the GWP associated to bio-jet fuel thought out system expansion. Other residues or wasted produced in the processes were assumed as zero impact ones due to the allocation was performed over the mentioned byproducts exclusively.

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## 6. Conclusions

- At the agricultural stage, three factors show higher influence over emissions variability: seed and straw yield, fertilizers applied, and diesel consumption, these two are the inputs to take under control to reduce the environmental burden associated to bio-jet fuel produced in Bologna and Pisa. Furthermore, Diesel consumption in Bologna has represent over 50% of GHG in every crop. Making it the input to put under control to reduce GHG.
- In general, using Crambe, Cartamo and Flax oils lead to a considerable reduction of environmental impacts compared with fossil jet fuel (considering production at Bologna). Furthermore, Flax is the best crops to be used in any site tested, from an environmental point of view. However, Cartamo has the best environmental performance in Bologna it seems statistical like Flax. It is due the greatest seed yield.
- In Pisa the results were different, using Camelina and Flax oils lead to a considerable reduction of environmental impacts compared with fossil jet fuel. Furthermore, Flax is the best crops to be used in any site tested, from an environmental point of view. On the other hand, Cartamo has the worst environmental performance in Pisa.
- Beyond the environmental assessment, using Flax may lead to a real reduction in GHG emission jointed with a less energy investment due to use of bio jet fuel in commercial ventures. Further research is needed.
- In the last few years, it is important to point out new perspectives in green chemistry to revalue the flax by-products (seeds and straw) as feedstock.
  In our case, non-wood pulp derived from Flax straw represents an opportunity in order to replace conventional wood pulp in Italian paper industry due to its better environmental performance (Bologna crops).

- Camelina Cartamo, Crambe and Flax are oilseed crops with short growth cycle, high oil content and low agronomic inputs requirements, recognized as good feedstocks for bio-refinery. The LCA results have shown that Camelina Jet fuel from Pisa reduces GHG emission compared with Bologna, fossil jet fuel and RED recommend. As by-product, Camelina meal has shown prospective applications as: i) animal feed, replacing soy meal; ii) Biogas, as feedstock; and iii) used as fertilizer. However, these uses should be assessed in order to make a feasible environmental balance of its potential reduction or increasing of GHG emission in the system. Nowadays, green chemistry has opened up new interest for arousing a comprehensive valorization of all integrated biorefinery by-products. When these products are raw materials providing an opportunity to replace highly polluting chemical, i.e. chemical origin N-fertilizer, pesticides and coal.
- In the last few years, Camelina and Flax derived biofuels production has been described very well. However, it is important to point out new perspectives in green chemistry for use and revaluing the Camelina and Flax oils as feedstock. One of them is the potential use as feedstock to produce biopolymers with press-sensitive adhesion applications. Another remarkable use of cold-pressed Camelina oil is as food oil due it Omega-3 profile and its high smoke point similar to linseed oil. Actually, there is a lack of productive and economic information in order to assess the alternative potential uses and the environmental impacts of Camelina oilseeds cultivated in Mediterranean zone.

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