

VALORIZATION OF BY-PRODUCTS AND RAW MATERIAL INPUTS IN THE BIOFUEL INDUSTRY

Report from an f3 project

Author:

Michael Martin, Environmental Technology and Management. Linköping University

PREFACE

This report is the result of a cooperation project within the Swedish Knowledge Centre for Renewable Transportation Fuels (f3). The f3 Centre is a nationwide centre, which through cooperation and a systems approach contributes to the development of sustainable fossil-free fuels for transportation. The centre is financed by the Swedish Energy Agency, the Region Västra Götaland and the f3 Partners, including universities, research institutes, and industry (see www.f3centre.se).

Special appreciation is acknowledged to the reference group, including Perstorp and Lantmännen Energi for their help with this report.

This report should be cited as:

Martin, M., (2013) *Valorization of by-products and raw material inputs in the biofuel industry*. Report No 2013:33, f3 The Swedish Knowledge Centre for Renewable Transportation Fuels, Sweden. Available at www.f3centre.se.

SUMMARY

As biofuel production increases worldwide, the market value for by-products has continued to change. By-products originally having strong market value may become saturated in the market with lower profitability. The use of these by-products for innovative products may therefore alleviate economic and environmental pressure for the commercial biofuel industry.

There are many potential useful substances that can be extracted from the by-products from the biofuel industry. Their subsequent uses can include for example use as feed, chemicals, energy, etc. Moreover, further value can be added to the raw material inputs by cascading their use for new products prior to use in biofuel production.

This report aims at identifying possibilities for the biofuel industry to add value to their product outputs in addition to cascading use of raw materials for increased valorization, with special attention devoted to the ethanol and biodiesel industry.

The report outlines different possibilities to extract proteins, carbohydrates, vitamins, amino acids from the by-products in addition to their use as chemical building blocks for other processing technologies. Raw materials used for the production of biofuel have also been identified as possible inputs to a variety of biorefinery systems. While there are many options available for valorization of the commercial biofuel industry, the promotion of advanced biofuels, environmental performance guidelines, market acceptance and competitiveness may be barriers to improving the current biofuel production performance.

SAMMANFATTNING

Produktionen av biodrivmedel har ökat över hela världen samtidigt som marknadsvärdet för biprodukter från dessa processer har förändrats. Utbudet av biprodukter som det från början var en stark efterfrågan på, möts nu av en mättad marknad och lägre lönsamhet. Detta trots att användningen av dessa biprodukter för innovativa ändamål inom biodrivmedelssektor kan förbättra den ekonomiska och miljömässiga prestandan avsevärt.

Det finns många potentiellt nyttiga ämnen som kan extraheras ur biprodukter från biodrivmedelsindustrin och som kan komma till användning på en rad områden såsom foder, kemikalier, energi m.m. Dessutom kan ytterligare värden plockas ut ur dessa råvaror genom att de används i produktionen av biobränsle, så kallad kaskadanvändning.

Givet alla dessa i dagsläget outnyttjade potentialer, syftar denna rapport till att identifiera möjligheter för biodrivmedelsindustrin att öka värdet på sina biprodukter. Särskild uppmärksamhet ägnas åt etanol- och biodieselindustrin i Sverige. Förutom att beröra användning av biprodukter från biodrivmedelsindustrin som kemiska byggstenar till andra processtekniker, och som möjliga råvaror i olika typer av bioraffinaderier, beskriver rapporten olika möjligheter att utvinna proteiner, kolhydrater, vitaminer och aminosyror ur biprodukterna.

Samtidigt som det finns många alternativ för valorisering i den kommersiella biodrivmedelsindustrin, finns det ofördelaktiga riktlinjer för miljöprestanda samt en bristande marknadsacceptans och konkurrenskraft som utgör hinder för att förbättra den nuvarande biodrivmedelsproduktionens prestanda. Även om rapportens tyngdpunkt ligger i att undersöka tekniska möjligheter, avser den avslutningsvis att även kartlägga dessa hinder som står i vägen för utvecklandet av en tekniskt avancerad biodrivmedelsproduktion.

CONTENTS

1	INTRODUCTION	6
1.1	AIMS AND SCOPE.....	6
1.2	METHOD	7
2	ETHANOL PRODUCTION VALORIZATION	9
2.1	STRAW	9
2.2	WHEAT GRAIN AND BRAN	10
2.3	ETHANOL-DDGS.....	11
2.4	CO ₂ CAPTURE FROM FERMENTATION	12
3	BIODIESEL VALORIZATION	13
3.1	INPUTS: RAPESEED MEAL AND RAPESEED OIL.....	13
3.2	GLYCEROL FROM BIODIESEL PRODUCTION.....	14
4	DISCUSSION	16
4.1	PROMOTION OF ADVANCE BIOFUEL PRODUCTION	16
4.2	ECONOMIC ISSUES	16
4.3	FOOD AND FEED MARKET	16
4.4	ENVIRONMENTAL IMPACTS	17
4.5	INTEGRATING WITH OTHER INDUSTRIES	17
4.6	ADDED VALUE PRODUCTS IN THE BIOECONOMY	18
5	CONCLUSIONS	19
5.1	FUTURE RESEARCH.....	19
	REFERENCES.....	20

1 INTRODUCTION

The production of biofuels has increased dramatically in the past ten years as nations worldwide continually increase their consumption and production to meet directives on the use of renewable fuels in the transportation sector. In the European Union, the target is to have 10% renewable fuels in the transportation sector by 2020 (European Commission, 2008), where Sweden has taken a strong position of introducing biofuels, especially ethanol and biodiesel to a lesser extent. Despite the optimism for biofuels in the transportation sector, the scientific community has increased its criticism on the production of biofuels including debates on the competition with food crops, land availability and energy requirements (Ponton, 2009; Timilsina and Shrestha, 2011). Directives have therefore included sustainability criteria to ensure biofuels are produced in a sustainable manner (European Union, 2009b). Biodiesel and ethanol production plants in Sweden meet these requirements and have sold large quantities of biofuels, primarily for low blending with diesel and gasoline respectively. Nonetheless, biofuel producers have been hindered by increasing raw material costs and limited markets for biofuels and by-products.

With the increased production of biofuels worldwide, the market for biofuel by-products has also changed. While the markets for biofuel by-products were originally strong, e.g. for raw glycerol and Distillers Dried Grains with Solubles (DDGS), the saturation of the market with these products has lowered their profitability and has changed the playing field for their use (Taheripour et al., 2010). A feasible way to improve the economics of the biodiesel and ethanol industries are to valorize the by-products (Fastinger et al., 2006; Gibreel et al., 2011; Vlysidis et al., 2011) to diversify the products and alleviate economic and environmental pressure for the commercial biofuel industry.

While the profitability has been reduced for the by-products for conventional purposes, the reduced prices and large volumes provide potential for increased valorization¹ of these materials to unlock the hidden value in these materials for improved economic and environmental performance. It is therefore essential to develop new technologies to provide sustainable solutions for the biofuel industry (Rodrigues et al., 2012). Many potential useful substances can be extracted from the by-products for use as feed, chemicals, energy, etc. (Martin et al., 2012; ElMekawy et al., 2013). Increased valorization could be accomplished in the biofuel industry to cascade production processes, add further value to the raw material inputs and produce an array of products to add value to the system through the use of by-products and cascading of raw materials.

1.1 AIMS AND SCOPE

The aim of this report is to identify possibilities for the biofuel industry to add value to their product outputs in addition to cascading use of raw materials for increased valorization. The report will therefore identify possible uses for the by-products and cascading possibilities for raw material inputs and other wastes fractions from the biofuel industry to improve the environmental and economic performance.

¹ According to ElMekawy et al. (2013) valorization can be defined as “the transformation of byproducts to alternative fuels, energy and other useful chemicals, with specific attention for sustainability and environmental objectives.”

The project has been accomplished by benchmarking developments and processes in the commercial biofuel industries and reviewing scientific literature for further possibilities. As such, the project does not take into account advanced biofuel production (e.g. lignocellulosic, gasification and other biofuel production processes) in addition to biogas production due to limited time and to provide results directed toward commercial biofuel producers in Sweden. Furthermore, the production of HVO is not included and the use of the biofuels (i.e. ethanol and biodiesel) in other industries or for other applications than vehicle fuels is not included. Detailed descriptions of the processes to refine products are not included in this report, and further information on these is directed to the references provided.

1.2 METHOD

In order to identify the possibilities for valorization of biofuel production processes, the project included a questionnaire and literature review. Prior to the literature review a questionnaire was conducted with experts from ethanol and biodiesel producers. The questionnaire was used to guide the literature review based on the processes, raw materials, by-products and possibilities identified by the biofuel producers. Thereafter benchmarking of state of the art production practices and possibilities from the literature was used to identify uses of by-products or process optimization for improvements in the use of raw materials for the commercial biofuel industry.

1.2.1 Questionnaire

A questionnaire was sent to experts at Lantmännen Agroetanol AB and Perstorp to understand more about the production processes, raw material inputs and by-products. The questionnaires also included questions on possibilities for optimization and adding value; see the following questions.

Raw Materials

- What are your primary raw materials for your production process?
- Is there any pre-processing?
- Can you envision methods to add more value to the raw material inputs?
- How would this happen?
- Do you have any current projects to add value or optimize the use of raw materials in your process?
- What obstacles would you meet to allow for this to happen?

By-Products

- What are your current by-product streams and products?
- Could the by-products be used another way?
- How could you add value to the by-products?
- Is there a trade-off with environmental performance and economic performance?
- Do you have any current projects to add value or optimize the output of by-products in your process?
- What obstacles would you meet to allow for this to happen?

1.2.2 Literature Review

In order to find relevant literature on the valorization of raw materials and by-products of biofuel production, a literature review was conducted. This was accomplished by reviewing key word combinations to find relevant articles with possibilities for valorization for scientific articles published between the years 2007-2013, similar to the approach of Martin et al (2012). The keywords included bioethanol, biodiesel and biogas in combination with added-value, cascading, valorization. The search resulted in a large number of articles with limited relevance for the study. A secondary search was then included to identify further possibilities through a scientific literature review based on the answers to questionnaires from Swedish ethanol and biodiesel producers as keyword searches. This was based on their answers of raw material inputs and by-products from the process which were used to find possibilities for valorization.

All key word searches for the original search and a selection of the secondary search can be found in Table 1 and Table 2. The method provided a good variety of possibilities, though may be limited to only those articles directly related to key-word searches.

Table 1. Key-word search word combinations.

Original Search	
Added value	Ethanol
	Biodiesel
Cascading	Ethanol
	Biodiesel
Valorization	Ethanol
	Biodiesel

Table 2. A selection of Keyword Searches from the Secondary Keyword Search.

Secondary Search	
Glycerol	Biodiesel
	Synthesis
Stillage/DDGS +	Protein
	Feed
Rapeseed Oil	Processing
	Nutrients
	Upgrading
	Refining
Bran	Protein
	Nutrients
	Upgrading
	Refining
Biorefinery	Straw
	Cereal
CO ₂	Capture
	Synthesis
Protein	DDGS
	Rapeseed/Oil cake
	Extraction

2 ETHANOL PRODUCTION VALORIZATION

In a Swedish perspective, grains are primarily used for the commercial ethanol production industry. This includes primarily wheat, but also additions of triticale and barley (Lantmännen Agroetanol AB, 2013). At the ethanol plant the grains are milled into a flour to allow enzymes to transform the starch into sugars. Water is thereafter mixed with the flour, producing a mash solution. The solution is thereafter heated and yeast is included to produce alcohol, releasing CO₂ in the process. The solid and liquid fractions are then separated and the liquid solution is then distilled to separate ethanol. The solid fraction is dried to produce distillers dried grain with solubles (DDGS). A representation of the different production steps is included in Figure 1 below.

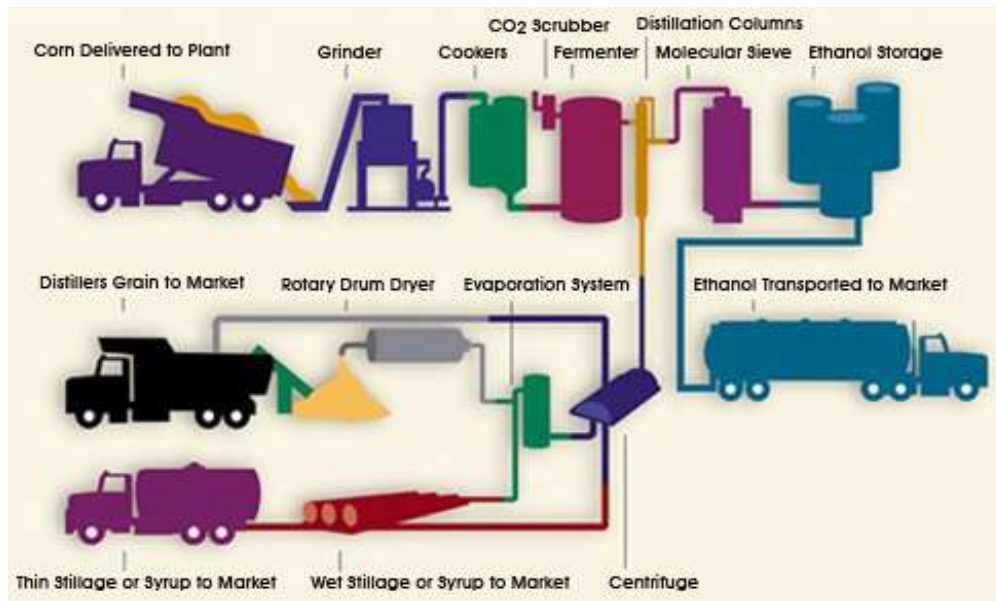


Figure 1. Ethanol Production Process Steps from Grains. Source: Indiana Ethanol Producers, 2013

2.1 STRAW

Although wheat straw is not necessarily a product of the bioethanol production process or a typical input, the potential for the use of the straw has many applications and was identified in many studies to take advantage of the lignocellulose available.

Agricultural residues, such as wheat and barley straw, have been identified in a number of studies as an important and potential input for biorefinery systems for the production of lignocellulosic ethanol and other chemicals (Sun and Chen, 2008; Talebnia et al., 2010; Briones et al., 2012; de Wild et al., 2012; Panagiotopoulos et al., 2013; Wang et al., 2013; Qureshi et al., In Press). Ethanol production from the straw is a general trend in these articles, although hydrogen, biogas, platform chemicals, polyols, polyurethane, bio-oil and heat and electricity were also identified as possible products from these biorefineries using the cellulose and lignin fractions; see Figure 2.

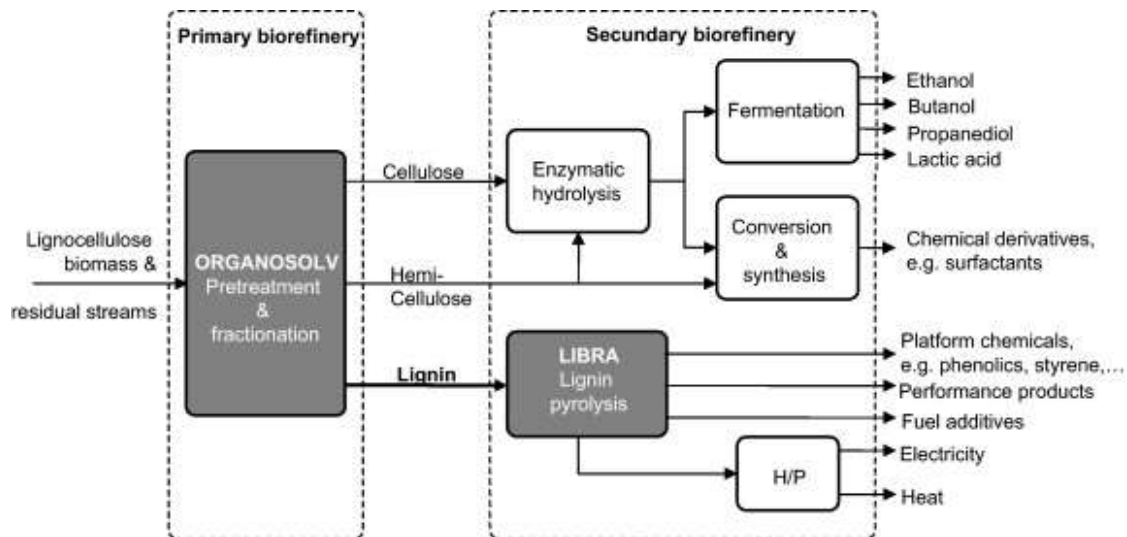


Figure 2. Products from a Lignocellulosic Biorefinery using Wheat Straw. Source: de Wild *et al.*, 2012.

2.2 WHEAT GRAIN AND BRAN

Wheat and other cereal kernels contain a variety of valuable fractions which can be separated to add value to the ethanol production process; see Figure 3 below. Wheat bran is one product which is present in large quantities, making up roughly 14-19% of the wheat grain. The bran is not typically separated in ethanol production processes and is often carried throughout the process and included in the DDGS to include fiber in the feed. Wheat bran has been identified as a potential input for biorefinery processes to produce additives for food, feed, pharmaceuticals and energy through enzymatic hydrolysis and hydrothermal pretreatment of the bran (Dorado *et al.*, 2009; Reisinger *et al.*, 2013; Apprich *et al.*, 2014).

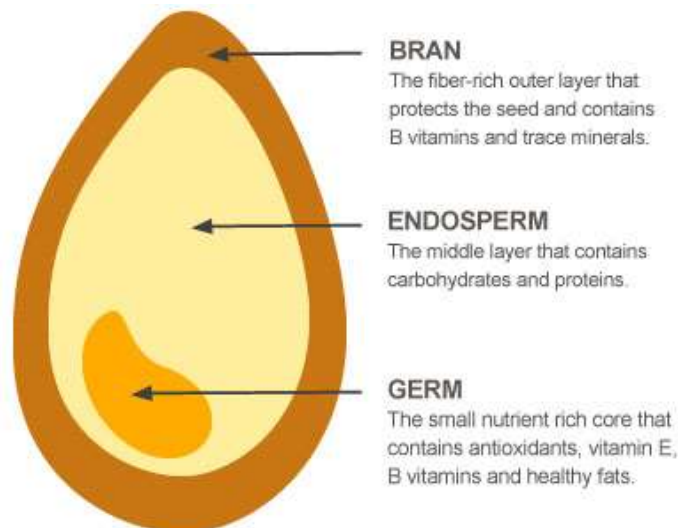


Figure 3. Composition of a Kernel of Wheat. Source: Wheat Foods Council, 2013.

Bran from cereals such as wheat has been identified in a number of studies as a potential source for many substances used as additive for food and feed. Apprich *et al.* (2014) have produced a valuable overview of the possibilities for valorization of wheat bran. This includes a number of sources for the food and feed industries and reviews of the processes and technologies to produce these substances. Table 3 below lists a selection of these substances and their uses. Apprich *et al.* (2014)

identified the use of wheat bran carbohydrates for the production of lactic acid, succinic acid, β -Glucan and Arabinoxylan used as preservative, flavoring agent, acidulant, dietary fiber supplement and functional food additives. Additionally wheat bran can be used to produce vanillin, protein, amino acids, oil and ferulic acid for food additives, flavoring and anti-oxidants. Wheat bran was even recognized as a filler in foods, e.g. to replace fats in sausages to provide fiber and a “filling sensation,” as identified by Vuholm et al. (2014).

Table 3. Wheat Bran Valorization Substances. Source: Apprich et al., 2014

Substance	Use	Source
Lactic Acid	Acidulant, Preservative, Flavor	Wheat Bran Carbohydrate Fraction
Succinic Acid	Acidulant, Preservative, Flavoring Agent	Wheat Bran Carbohydrate Fraction
β -Glucan	Functional Food Ingredient	Wheat Bran Carbohydrate Fraction
Arabinoxylan	Dietary Fiber Supplement	Wheat Bran Carbohydrate Fraction
Furfural and 5-Hydroxymethylfurfural	Substitutes for petroleum-based building blocks in the production of fine chemicals, fuels and polymers	Wheat Bran Carbohydrate Fraction
Vanillin	Flavor in food and beverages, fragrance	Non-Carb Fraction
Protein	Food/feed additive	Non-Carb Fraction
Amino acids	Food/feed additive	Non-Carb Fraction
Wheat bran oil	Food/feed additive	Non-Carb Fraction
Ferulic acid	Anti-oxidant	Non-Carb Fraction

Wheat bran can also be used as a possible source of xylooligosaccharides through microwave assisted enzymatic hydrolysis. Xylooligosaccharides are used in pharmaceutical preparations for their antiallergy, antimicrobial, anti-infection and anti-inflammatory properties (Wang and Lu, 2013).

2.3 ETHANOL-DDGS

Ethanol producers produce a large volume of stillage which is dried to obtain distillers dried grains with solubles (DDGS). Currently DDGS is primarily used as an animal feed for cattle and pigs as it contains a large percentage of protein, fiber, antioxidants and other nutrients, roughly two to three times the amount as grains (Gibreel et al., 2009; Gibreel et al., 2011). Many of these are important for dietary nutrition to with important health benefits. As such, the availability is greatly increased and concentrated in the DDGS providing potential for valorization of new products. Through the use of new enzymes Gibreel et al. (2011) identified the possibilities of DDGS from wheat and triticale ethanol production to produce Vitamin E containing compounds such as trionels, tocopherols, dietary fibers such as β -glucan in addition to essential fatty acids such as linoleic acid.

DDGS has also applications as an aquaculture feed; though less than 1% of DDGS is used as such, primarily from the corn ethanol industry (Shurson, 2012). The aquaculture industry has nonetheless grown to meet increasing demands for food, and thus a demand for feed resources has followed suit. DDGS has therefore been explored in many studies as an alternative source of protein from fish meal as an aquaculture feed with positive results when blended with traditional fish meal (FAO, 2012; Øverland et al., 2013).

Further value could be obtained from the DDGS by separating the fraction of protein in the DDGS in order to producer higher value protein products. Through the sieving of DDGS from wheat ethanol production, fractionation of different particle sizes can yield fractions of DDGS with varying degrees of crude proteins (Randall and Drew, 2010).

DDGS has also been identified as a “cheap” source of carbon for the production of biopolymers for use in the food, pharmaceutical and cosmetic industries. Though the less energy intensive production of biopolymers produced by the DDGS, polyesters, poly alcohols and polysaccharides can be produced (ElMekawy et al., 2013). ElMekawy et al. (2013) also describe the use of DDGS as an inexpensive source for the fermentative production of organic acids, lactic acid in particular, which are used for pharmaceutical, chemical, food, textile, leather cosmetic and polymer industries.

2.4 CARBON DIOXIDE (CO₂) CAPTURE FROM FERMENTATION

In the fermentation process, sugars are converted to alcohol and CO₂. Typically, ethanol plants release the CO₂ to the atmosphere, which results in a waste product. However, by capturing this CO₂, further economic profitability can be accomplished as the CO₂ from fermentation can have high levels of purity (Xu et al., 2010; Pontzen et al., 2011; Olajire, 2013).

CO₂ has many industrial applications, especially in the food industry, where it is used for carbonation for beverages, packaging and cooling. It can also be used as a refrigerant, supercritical solvent and an inert gas. As the CO₂ from fermentation processes come from biological sources, it can also be used as a green source of carbon compared to conventional production processes from e.g. the production of hydrogen and ammonium fertilizers. Techniques such as pressure swing adsorption and cryogenic distillation can be used to capture the CO₂ from ethanol production for further processing (Olajire, 2010; Filho et al., 2013). Several authors have identified CO₂ for the green synthesis of organic carbonates using new catalysts, such as ionic liquids, in place of toxic raw materials to make the process more environmentally benign; see (Sun et al., 2005). CO₂ has also been identified as a source for the production of other fuels such as methanol (Pontzen et al., 2011). The use of CO₂ from the fermentation process, in its unfiltered form, in greenhouses and for the production of algae is also an option (Jaffrin et al., 2003; Doušková et al., 2010; Zeng et al., 2011).

3 BIODIESEL VALORIZATION

Biodiesel production in Sweden is dominated by the use of rapeseed (RME) (Energimyndigheten, 2013), while other oils and fats are used to produce biodiesel, including waste oils and fats in smaller scale production processes. Biodiesel is produced through the transesterification process where oil is mixed with a catalyst and an alcohol to remove the triglyceride molecule and produce methyl ester chains. Typically fossil based methanol is used as the alcohol for this process, though bio-based methanol can also be used e.g. in the Verdis Polaris Aura (Perstorp, 2013). The process produces fatty acid methyl ester (FAME or biodiesel) and crude glycerol, both of which can be washed and refined for higher purity. Figure 4 below describes the process used at Perstorp. The descriptions provided in subsequent text are related primarily to the use of rapeseed oil for biodiesel production from a Swedish perspective.

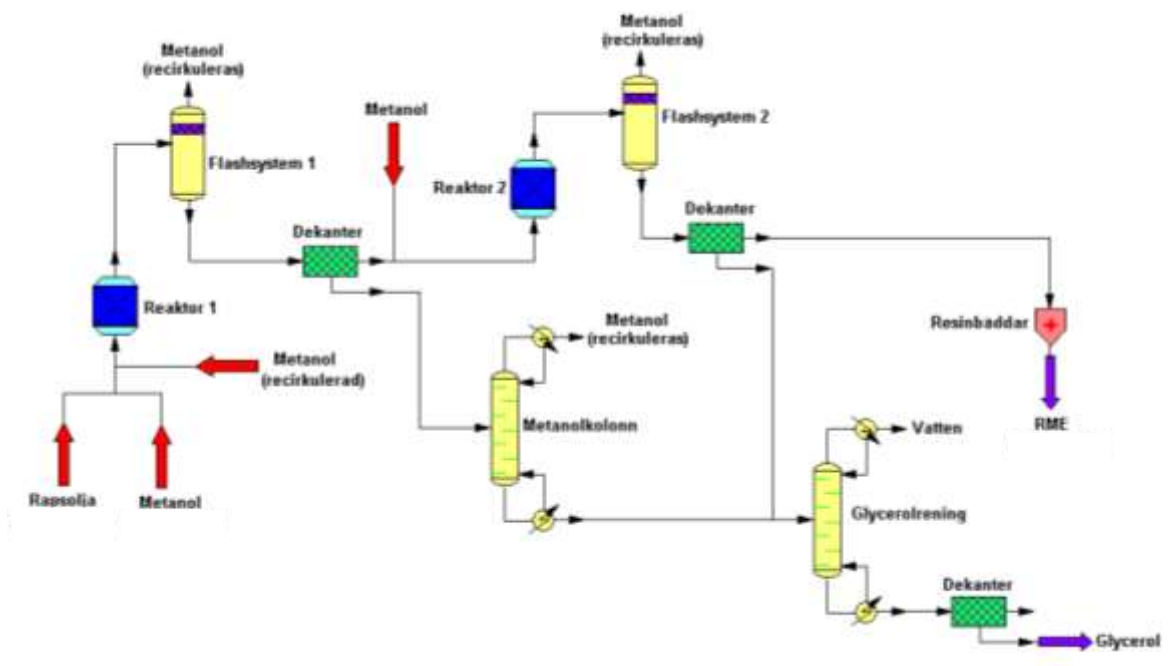


Figure 4. RME Production at Perstorp. Source: Perstorp, 2013.

3.1 INPUTS: RAPESEED MEAL AND RAPESEED OIL

The production of biodiesel begins with the pressing of oil seeds to obtain oil which is used for food production and also biodiesel production. The major by-product from the pressing is a defatted meal which contains valuable proteins and carbohydrates. This rapeseed cake is of considerably lower commercial value when compared to e.g. soy meal. However, through valorization of the meal, the economic and environmental sustainability of the biodiesel production market may be improved (Rodrigues et al., 2012).

3.1.1 Rapeseed Meal

Rapeseed meal is typically used as an animal feed for pork production (FAO, 2012). In the future it is possible that the rapeseed meal can also be used for applications in food products for humans, fish food and other innovative processes. The meal contains a fraction of protein that can be concentrated and isolated to produce high value protein products. Through protein hydrolysis, peptides

and essential amino acids can be obtained. Furthermore, the nutritional value of the rapeseed meal can even be improved by removing glucosinolates, phylates and erucic acid, which significantly reduce the nutritional level of the rapeseed meal due to their toxic and anti-nutritional characteristics, making it possible for human consumption (Moure et al., 2006; Tripathi and Mishra, 2007; Rodrigues et al., 2012). This is equally important for the use of rapeseed as a fish food (Nagel et al., 2012). Carbohydrates which can cause flatulence in humans and animals, e.g. mono saccharides and oligosaccharides, can be separated using an alcohol solution making the rapeseed meal more nutritional. Furthermore, carbohydrates can also be hydrolyzed to sugars to produce ethanol through fermentation (Rodrigues et al., 2012).

3.1.2 Rapeseed Oil

Rapeseed oil, like other oils from oil seed crops and palm oil contains many vitamins and valuable nutrients, e.g. Vitamin E. In the palm oil industry, vitamins are extracted before further processing into biodiesel (Othman et al., 2010). Vitamin E is present in rapeseed oil at an amount of 4-7% in the fatty acid distillate (Preedy and Watson, 2007). The removal of antioxidants such as vitamin E has also been recognized to improve the oxidative stability of biodiesel (Vasudevan and Briggs, 2008) and thus provide further value to both the biodiesel and antioxidants.

3.2 GLYCEROL FROM BIODIESEL PRODUCTION

With the rapid increase in biodiesel production in the past few years, the price of glycerol has decreased substantially, allowing for glycerol to emerge as an important chemical building block for other processes (Johnson and Taconi, 2007). Many potential processes can be made use of to further develop markets for glycerol and a large number of uses for glycerol, crude and refined, have been identified in the literature (Martin et al., 2012).

The use of glycerol to produce pharmaceuticals and chemicals or as a building block for chemical production is abundant in the literature with applications for glycerol for use in microbiology processing to polymer production. Glycerol has been identified as a valuable source for industrial microbiology (da Silva et al., 2009) with products such as propylene glycol, propionic acid, acrylic acid, propanol, isopropanol, allyl alcohol and acrolein identified as suitable due to their price differentials and market capacity (Johnson and Taconi, 2007). Many of these chemicals are currently produced from fossil fuels and with increasing prices of fossil fuels, the applicability for the production from crude glycerol may become increasingly interesting. Glycerol has also been identified for the production of lactic acid, butanol and succinic acid (Yazdani and Gonzalez, 2007; Vlysidis et al., 2011). Metabolites and glycolipids may also be produced from glycerol (Liu et al., 2011; Abad and Turon, 2012). Plastic/polymer production from glycerol has also been identified in the literature (Cavalheiro et al., 2009).

Glycerol has been identified in several studies as for the production of energy and as a fuel additive to gasoline and diesel (Fernando et al., 2007; Kiatkittipong et al., 2010). Butanol is one such additive to improve the properties of gasoline and diesel with its higher octane number, lower vapor pressure and heat of vaporization. Glycerol has even been proposed as a fuel for combustion engines directly (McNeil et al., 2012). The addition of glycerol to biogas production processes in combination with other substrates has been identified in several studies (Yazdani and Gonzalez, 2007; Fountoulakis and Manios, 2009; Siles López et al., 2009) and is currently in practice in many

Swedish production plants (Svensk Biogas AB, 2013). Hydrogen may also be produced from glycerol through steam reformation (Slinn et al., 2008; Sánchez et al., 2010).

Lastly, glycerol has many applications in the feed industry where it is used as an animal feed (Johnson and Taconi, 2007; Donkin et al., 2009). Glycerol has also been identified as a source for fish feed (FAO, 2012) In the food industry glycerol can be used to produce triacetin, a comestible oil, for food addtives and flavorings (Bonet et al., 2009; Liao et al., 2009). Polyunsaturated fatty acids can also be produced using glycerol (Abad and Turon, 2012).

4 DISCUSSION

With the increase in biofuel production and even larger shares required to meet legislation in the future, the by-products from biofuel production processes will become available at a larger extent in the market. As an increase in their volumes will take place, these products from biofuel processes may also offer cost-effective alternatives to fossil products. The literature review has outlined many potential applications for by-products from biofuel production processes which may provide added-value for commercial biofuel producers.

4.1 PROMOTION OF ADVANCE BIOFUEL PRODUCTION

While biofuel production and consumption is set to increase, advanced production methods are currently receiving increased attention (Taylor, 2008; Cherubini, 2010; Fahd et al., 2012). Legislation in both the US and Europe promote the use of advanced biofuel production, e.g. gasification and lignocellulosic biofuel production (USA Law, 2007; European Commission, 2008; European Union, 2009b). European directives even allow for double-counting of production figures and improvements from advanced biofuels (Bole and Londo, 2010). This may therefore have implications on the production of biofuels using commercial technologies and traditional crops, i.e. grains and oil-seeds. In order to compete with advanced biofuel production, the commercial biofuel industry may therefore need to improve their economic and environmental performance in the future (Martin, 2013). Nonetheless, advanced biofuel production remains unproven and immature at the commercial scale due to the uncertainty associated production costs, warranting environmental performance and energy efficiency difficult (Srirangan et al., 2012; Wetterlund, 2012).

4.2 ECONOMIC ISSUES

Many of the reports from literature review are related to possibilities for specific extractions from by-products and other materials from the biofuel industry. These reports and articles may therefore be applicable only to lab scale or pilot scale systems. The commercialization of these processes however may require advanced processing and continued technological innovation support from a variety of actors (Haase et al., 2013). ElMekawy et al. (2013) also state that the scaling up from the lab or pilot scale is limited by the standardization of the production process at the industrial scale.

Several of the reports found in the literature require the use of special enzymes, which may have large costs. The contribution of enzyme costs to the economy of biotechnology and biofuel production is currently a debated issue in the scientific literature. While some authors assume that the costs will decrease with technological innovation and increased production, others see the costs as a barrier for the processes; see e.g. (Merino and Cherry, 2007; Klein-Marcuschamer et al., 2012). Therefore, the economic and energy inputs for these new systems must be accounted for when determining the possibility for valorization.

4.3 FOOD AND FEED MARKET

With a growing world population, the demand for protein sources to replacing and substituting expensive sources of animal protein may become more apparent in the near future. It was shown that rapeseed meal and protein fractions from wheat bran and DDGS may be used to provide protein sources for food production for not only animals but also humans (Rodrigues et al., 2012) though a large share of biofuel production by-products are used for animal feed (FAO, 2012). In order to

allow for the proteins and other fractions from biofuel by-products to be used for human consumption applications, concerns on the amount of yeast, bacteria and whether the biofuel producers are accepted for food grade production will need to be addressed (FAO, 2012). Once biofuels production by-products begin producing more products for human dietary nutrition, some of the debate on food vs. fuel (Srinivasan, 2009; Tilman et al., 2009) may diminish. Nonetheless, by producing may also be a tradeoff between using the by-products for human food versus a low cost fodder as the consumption patterns of meat and dairy continue to rise worldwide (Fiala, 2008; Latvala et al., 2012). This may be especially important for farmers, e.g. from Lantmännen, the farmers' cooperative who own the Lantmännen Agroetanol production plant. Additionally, many commercial biofuel producers may not have responsibility or ownership of the pre-processing of raw materials which are used in their processes, e.g. wheat production and the use of the straw as well as rapeseeds and meal. Therefore, added value for these products may, if not associated with the biofuel producer, not lead to improvements for the biofuel plants themselves.

4.4 ENVIRONMENTAL IMPACTS

With an increase in biofuel production by-products, the substitution of conventional products may have important implications on the environmental performance of biofuel production and other systems. In several studies, it has been identified that the substitution of protein fodder by biofuel production by-products has important environmental performance improvements for biofuel production systems (Börjesson et al., 2010; Börjesson and Tufvesson, 2010; Taheripour et al., 2010; Martin, 2013; Martin et al., 2014). Through the upgrading of proteins from e.g. DDGS and rapeseed meal for use as a dietary protein source which directly substitutes animal protein may have larger improvements compared to substituting it for protein feed. Environmental performance improvements may also take place for biofuel producers when products from the biofuel systems substitute fossil based raw materials. Examples as such include CO₂, polymers, etc. The improvement possibilities from by-products and other value added products from biofuel processes may be one way to meet the greenhouse gas emission reduction limitations of 50% and 60% compared to fossil systems for the years 2017 and 2018 respectively (European Union, 2009a). If indirect land use (iLUC) changes are to be taken into account in the greenhouse gas calculations, these credits may allow for the biofuels to continue to meet the thresholds for sustainable fuels. This is especially important for biodiesel production, which may have difficulties meeting the greenhouse gas emission reductions if iLUC emissions are included (Börjesson et al., 2013). Under the current rules for life cycle emissions accounting however, credits may not be included for by-product production, though the scientific community is keen on making this possible (Martin, 2013). Tradeoffs with the environmental performance may also take place, when the traditional methods offer more benefit than the new value-added systems (Martin et al., 2014; Martin et al., In Press).

4.5 INTEGRATING WITH OTHER INDUSTRIES

One way to alleviate the economic “burden” of introducing a new process to valorize by-products may be to integrate production processes with other industries. Co-location and other forms of industrial symbiosis may offer benefits such as reduced material and energy consumption (Martin and Eklund, 2011; Martin et al., 2012). Several authors have outlined the possible improvements which can be accomplished by making use of by-products and using renewable energy systems (Börjesson, 2004; Murphy and McCarthy, 2005; Murphy and Power, 2008; Martin et al., 2014). Improved environmental performance can result from integration with other industries to make use

of by-products and (Sokka et al., 2011; Martin et al., 2014). A large share of the greenhouse gas emissions reduction from the ethanol plant of Lantmännen Agroetanol can be attributed to the use of renewable steam from the neighboring combined heat and power plant (Cleantech Östergötland, 2009; Lantmännen Agroetanol AB, 2013; Martin, 2013; Martin et al., 2014).

4.6 ADDED VALUE PRODUCTS IN THE BIOECONOMY

The literature review has identified that the use of products and by-products from the biofuel industry may substitute conventional raw materials based on fossil fuels. As such, the biofuel industry may allow for a transition to regional bio-based systems with new innovative uses of the biofuel production by-products, although the extent to which may not be large world-wide, simply a substitute for a share of products. The use of biomass in such added value systems may therefore encourage sustainable economic growth as well as stimulate innovation (Ekman, 2012). Regionally, this could allow for a transition to a bioeconomy although certain obstacles must be overcome to allow added value products from bio-based sources to be included in the market. This may require new policies and conditions for their adaptation in the market, but also the products must be competitive with conventional products, including their function, price and properties (SP, 2013). It is thus important that the proposed “added-value” products or valorization through new products does exactly what it suggests; provide added revenue or improvements in both economic and environmental terms in order for them to be considered successful and sustainable.

5 CONCLUSIONS

This report has outlined a range of possible added-value products from the commercial biofuel industry, namely the ethanol and biodiesel industry. The results from the literature review outline the possibilities for added-value products from both by-products and raw material inputs for biofuel production. Examples of these include the use of by-products for use in further refinement processes to extract proteins, carbohydrates, vitamins, amino acids in addition to using the by-products as chemical building blocks for other processing technologies. The raw materials used for the production of biofuels, i.e. wheat and straw in addition to rapeseed and meal, have also been included and have been identified as possible inputs to a variety of biorefinery systems. Valorization of these products may be one method to allow the biofuel production industry to become more economically and environmentally sustainable although the promotion of advanced biofuels, environmental performance quantification guidelines and market acceptance and competitiveness may be barriers.

5.1 FUTURE RESEARCH

As outlined in the discussion, the use of products from biofuel production process in added-value processes may have implication on the economic and environmental performance for biofuel producers. Studies on the environmental improvements through the replacement of conventional products by biofuel production products and by-products may be a welcomed addition the biofuel production life cycle assessment literature. Furthermore, quantifications of the possibilities for economic improvements through these novel products are also necessary in order to identify if the processes can lead to valorization.

REFERENCES

- Abad, S., Turon, X., 2012. Valorization of biodiesel derived glycerol as a carbon source to obtain added-value metabolites: Focus on polyunsaturated fatty acids. *Biotechnology Advances* 30(3), 733-741.
- Apprich, S., Tirpanalan, Ö., Hell, J., Reisinger, M., Böhmendorfer, S., Siebenhandl-Ehn, S., Novalin, S., Kneifel, W., 2014. Wheat Bran-Based Biorefinery 2: Valorization of Products. *LWT - Food Science and Technology*
- Bole, T., Londo, M., 2010. The role of policy in mitigating risk of second generation biofuel projects. Elobio Policy Paper 6. Energy Research Centre of the Netherlands. Netherlands.
- Bonet, J., Costa, J., Sire, R., Reneaume, J., Pleşu, A.E., Pleşu, V., Bozga, G., 2009. Revalorization of glycerol: Comestible oil from biodiesel synthesis. *Food and Bioproducts Processing* 87(3), 171-178.
- Börjesson, P., Tufvesson, L., Lantz, M., 2010. Livscykelanalys av svenska biodrivmedel. Report No. 70. Environmental and Energy System Studies, Lund University. Lund, Sweden.
- Börjesson, P., Lundgren, J., Ahlgren, S., Nyström, I., 2013. Dagens och Framtidens Hållbara Biodrivmedel: Underlagsrapport från f3 till utredningen om FossilFri Fordonstrafik . f3 2013:13. f3-The Swedish Knowledge Centre for Renewable Transportation Fuels.
- Börjesson, P., 2004. Energianalys av drivmedel från spannmål och vall (Energy analysis of transportation fuels from grain and ley crops). IMES/EESS Report No.54. Lund University-Department of Technology and Society.
- Börjesson, P., Tufvesson, L.M., 2010. Agricultural crop-based biofuels – resource efficiency and environmental performance including direct land use changes. *Journal of Cleaner Production* 19 (2-3), 108-120.
- Briones, R., Serrano, L., Labidi, J., 2012. Valorization of some lignocellulosic agro-industrial residues to obtain biopolyols. *Journal of Chemical Technology & Biotechnology* 87(2), 244-249.
- Cavalheiro, J.M.B.T., de Almeida, M.C.M.D., Grandfils, C., da Fonseca, M.M.R., 2009. Poly(3-hydroxybutyrate) production by *Cupriavidus necator* using waste glycerol. *Process Biochemistry* 44(5), 509-515.
- Cherubini, F., 2010. The biorefinery concept: Using biomass instead of oil for producing energy and chemicals. *Energy Conversion and Management* 51(7), 1412-1421.
- Cleantech Östergötland, 2009. The Energy Complex at Händelö. *Cleantech Magazine-Environmental Technology in the Twin Cities of Sweden* 1, 16-17.
- da Silva, G.P., Mack, M., Contiero, J., 2009. Glycerol: A promising and abundant carbon source for industrial microbiology. *Biotechnology Advances* 27(1), 30-39.
- de Wild, P.J., Huijgen, W.J.J., Heeres, H.J., 2012. Pyrolysis of wheat straw-derived organosolv lignin. *Journal of Analytical and Applied Pyrolysis* 93(0), 95-103.
- Donkin, S.S., Koser, S.L., White, H.M., Doane, P.H., Cecava, M.J., 2009. Feeding value of glycerol as a replacement for corn grain in rations fed to lactating dairy cows. *Journal of Dairy Science* 92(10), 5111-5119.

- Dorado, M.P., Lin, S.K.C., Koutinas, A., Du, C., Wang, R., Webb, C., 2009. Cereal-based biorefinery development: Utilisation of wheat milling by-products for the production of succinic acid. *Journal of Biotechnology* 143(1), 51-59.
- Doušková, I., Kaštánek, F., Maléterová, Y., Kaštánek, P., Doucha, J., Zachleder, V., 2010. Utilization of distillery stillage for energy generation and concurrent production of valuable microalgal biomass in the sequence: Biogas-cogeneration-microalgae-products. *Energy Conversion and Management* 51(3), 606-611.
- Ekman, A., 2012. Environmental Assessment of Emerging Bio-based Production - Possibilities in a Future Bio-economy. *Environmental and Energy System Studies*, Lund University; Lund University.
- ElMekawy, A., Diels, L., De Wever, H., Pant, D., 2013. Valorization of Cereal Based Biorefinery Byproducts: Reality and Expectations. *Environmental science & technology* 47(16), 9014-9027.
- Energimyndigheten, 2013. Hållbara biodrivmedel och flytande biobränslen under 2012.
- European Commission, 2008. 20 20 by 2020: Europe's Climate Change Opportunity. *Communication COM (2008) 30*, 1-12.
- European Union, 2009a. amending Directive 98/70/EC as regards the specification of petrol, diesel and gas-oil and introducing a mechanism to monitor and reduce greenhouse gas emissions and amending Council Directive 1999/32/EC as regards the specification of fuel used by inland waterway vessels and repealing Directive 93/12/EEC. *Official Journal of the European Union*.
- European Union, 2009b. Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC. L140/16-62: *Official Journal of the European Union*
- Fahd, S., Fiorentino, G., Mellino, S., Ulgiati, S., 2012. Cropping bioenergy and biomaterials in marginal land: The added value of the biorefinery concept. *Energy* 37(1), 79-93.
- FAO ,2012. Biofuel co-products as livestock feed - Opportunities and challenges.
- Fastinger, N.D., Latshaw, J.D., Mahan, D.C., 2006. Amino acid availability and true metabolizable energy content of corn distillers dried grains with solubles in adult cecectomized roosters. *Poultry science* 85(7), 1212-1216.
- Fernando, S., Adhikari, S., Kota, K., Bandi, R., 2007. Glycerol based automotive fuels from future biorefineries. *Fuel* 86(17-18), 2806-2809.
- Fiala, N., 2008. Meeting the demand: An estimation of potential future greenhouse gas emissions from meat production. *Ecological Economics* 67(3), 412-419.
- Filho, R.B.d.A., Danielski, L., de Carvalho, F.R., Stragevitch, L., 2013. Recovery of carbon dioxide from sugarcane fermentation broth in the ethanol industry. *Food and Bioproducts Processing* 91(3), 287-291.
- Fountoulakis, M.S., Manios, T., 2009. Enhanced methane and hydrogen production from municipal solid waste and agro-industrial by-products co-digested with crude glycerol. *Bioresource technology* 100(12), 3043-3047.

- Gibreel, A., Sandercock, J.R., Lan, J., Goonewardene, L.A., Zijlstra, R.T., Curtis, J.M., Bressler, D.C., 2009. Fermentation of barley by using *Saccharomyces cerevisiae*: Examination of barley as a feedstock for bioethanol production and value-added products. *Applied and Environmental Microbiology* 75(5), 1363-1372.
- Gibreel, A., Sandercock, J.R., Lan, J., Goonewardene, L.A., Scott, A.C., Zijlstra, R.T., Curtis, J.M., Bressler, D.C., 2011. Evaluation of value-added components of dried distiller's grain with solubles from triticale and wheat. *Bioresource technology* 102(13), 6920-6927.
- Haase, R., Bielicki, J., Kuzma, J., 2013. Innovation in emerging energy technologies: A case study analysis to inform the path forward for algal biofuels. *Energy Policy* 61(0), 1595-1607.
- Indiana Ethanol Producers, 2013. Ethanol Production Processes, Dry Milling. Available At: http://indianaethanolproducers.org/dry_milling.html.
- Jaffrin, A., Bentounes, N., Joan, A.M., Makhlof, S., 2003. Landfill Biogas for heating Greenhouses and providing Carbon Dioxide Supplement for Plant Growth. *Biosystems Engineering* 86(1), 113-123.
- Johnson, D.T., Taconi, K.A., 2007. The glycerin glut: Options for the value-added conversion of crude glycerol resulting from biodiesel production. *Environmental Progress* 26(4), 338-348.
- Kiatkittipong, W., Suwanmanee, S., Laosiripojana, N., Praserttham, P., Assabumrungrat, S., 2010. Cleaner gasoline production by using glycerol as fuel extender. *Fuel Processing Technology* 91(5), 456-460.
- Klein-Marcuschamer, D., Oleskiewicz-Popiel, P., Simmons, B.A., Blanch, H.W., 2012. The challenge of enzyme cost in the production of lignocellulosic biofuels. *Biotechnology and bioengineering* 109(4), 1083-1087.
- Lantmännen Agroetanol AB, 2013. Available At: <www.agroetanol.se>. Accessed: Jan 10, 2013.
- Latvala, T., Niva, M., Mäkelä, J., Pouta, E., Heikkilä, J., Kotro, J., Forsman-Hugg, S., 2012. Diversifying meat consumption patterns: Consumers' self-reported past behaviour and intentions for change. *Meat Science* 92(1), 71-77.
- Liao, X., Zhu, Y., Wang, S., Li, Y., 2009. Producing triacetyl glycerol with glycerol by two steps: Esterification and acetylation. *Fuel Processing Technology* 90(7-8), 988-993.
- Liu, Y., Koh, C.M.J., Ji, L., 2011. Bioconversion of crude glycerol to glycolipids in *Ustilago maydis*. *Bioresource technology* 102(4), 3927-3933.
- Martin, M., 2013. Industrial Symbiosis in the Biofuel Industry: Quantification of the Environmental Performance and Identification of Synergies. PhD Thesis. Environmental Technology and Management. Linköping University.
- Martin, M., Eklund, M., 2011. Improving the environmental performance of biofuels with industrial symbiosis. *Biomass and Bioenergy* 35(5), 1747-1755.
- Martin, M., Svensson, N., Eklund, M., Fonseca, J., 2012. Production synergies in the current biofuel industry: opportunities for development. *Biofuels*. 5, 545-554
- Martin, M., Svensson, N., Eklund, M., In Press. Who gets the benefits? An approach for assessing the environmental performance of industrial symbiosis. *Journal of Cleaner Production*

- Martin, M., Svensson, N., Fonseca, J., Eklund, M., 2014. Quantifying the environmental performance of integrated bioethanol and biogas production. *Renewable Energy* 61(0), 109-116.
- McNeil, J., Day, P., Sirovski, F., 2012. Glycerine from biodiesel: The perfect diesel fuel. *Process Safety and Environmental Protection* 90(3), 180-188.
- Merino, S., Cherry, J., 2007. Progress and Challenges in Enzyme Development for Biomass Utilization, in: Olsson, L. (Ed.), . Springer Berlin Heidelberg, 95-120.
- Moure, A., Sineiro, J., Domínguez, H., Parajó, J.C., 2006. Functionality of oilseed protein products: A review. *Food Research International* 39(9), 945-963.
- Murphy, J.D., McCarthy, K., 2005. Ethanol production from energy crops and wastes for use as a transport fuel in Ireland. *Applied Energy* 82(2), 148-166.
- Murphy, J.D., Power, N.M., 2008. How can we improve the energy balance of ethanol production from wheat? *Fuel* 87(10-11), 1799-1806.
- Nagel, F., von Danwitz, A., Tusche, K., Kroeckel, S., van Bussel, C.G.J., Schlachter, M., Adem, H., Tressel, R., Schulz, C., 2012. Nutritional evaluation of rapeseed protein isolate as fish meal substitute for juvenile turbot (*Psetta maxima* L.) — Impact on growth performance, body composition, nutrient digestibility and blood physiology. *Aquaculture* 356–357(0), 357-364.
- Olajire, A.A., 2013. Valorization of greenhouse carbon dioxide emissions into value-added products by catalytic processes. *Journal of CO2 Utilization* 3–4(0), 74-92.
- Olajire, A.A., 2010. CO2 capture and separation technologies for end-of-pipe applications – A review. *Energy* 35(6), 2610-2628.
- Othman, N., Manan, Z.A., Wan Alwi, S.R., Sarmidi, M.R., 2010. A review of extraction technology for carotenoids and vitamin e recovery from palm oil. *Journal of Applied Sciences* 10(12), 1187-1191.
- Øverland, M., Krogdahl, Å., Shurson, G., Skrede, A., Denstadli, V., 2013. Evaluation of distiller's dried grains with solubles (DDGS) and high protein distiller's dried grains (HPDDG) in diets for rainbow trout (*Oncorhynchus mykiss*). *Aquaculture* 416–417(0), 201-208.
- Panagiotopoulos, I.A., Bakker, R.R., de Vrije, T., Claassen, P.A.M., Koukios, E.G., 2013. Integration of first and second generation biofuels: Fermentative hydrogen production from wheat grain and straw. *Bioresource technology* 128(0), 345-350.
- Perstorp, 2013. Available At: <<https://www.perstorp.com/en/Products/Fuels/Fuels>>. Accessed: November 10, 2013.
- Ponton, J.W., 2009. Biofuels: Thermodynamic sense and nonsense. *Journal of Cleaner Production* 17(10), 896-899.
- Pontzen, F., Liebner, W., Gronemann, V., Rothaemel, M., Ahlers, B., 2011. CO2-based methanol and DME – Efficient technologies for industrial scale production. *Catalysis Today* 171(1), 242-250.
- Preedy, V.R., Watson, V., ,2007. *The Encyclopedia of Vitamin E*, 960.

- Qureshi, N., Saha, B.C., Dien, B., Hector, R.E., Cotta, M.A., Production of butanol (a biofuel) from agricultural residues: Part I – Use of barley straw hydrolysate. *Biomass and Bioenergy*, In Press, Corrected Proof.
- Randall, K.M., Drew, M.D., 2010. Fractionation of wheat distiller's dried grains and solubles using sieving increases digestible nutrient content in rainbow trout. *Animal Feed Science and Technology* 159(3–4), 138-142.
- Reisinger, M., Tirpanalan, Ö., Prückler, M., Huber, F., Kneifel, W., Novalin, S., 2013. Wheat bran biorefinery – A detailed investigation on hydrothermal and enzymatic treatment. *Bioresource technology* 144(0), 179-185.
- Rodrigues, I.M., Coelho, J.F.J., Carvalho, M.G.V.S., 2012. Isolation and valorisation of vegetable proteins from oilseed plants: Methods, limitations and potential. *Journal of Food Engineering* 109(3), 337-346.
- Sánchez, E.A., D'Angelo, M.A., Comelli, R.A., 2010. Hydrogen production from glycerol on Ni/Al₂O₃ catalyst. *International Journal of Hydrogen Energy* 35(11)
- Shurson, J., 2012. Maize dried distiller's grains with solubles (DDGS) - a new alternative ingredient in aquafeeds. *World Aquac.* 43, 54-58.
- Siles López, J.Á., Martín Santos, María de los Ángeles, Chica Pérez, A.F., Martín Martín, A., 2009. Anaerobic digestion of glycerol derived from biodiesel manufacturing. *Bioresource technology* 100(23), 5609-5615.
- Slinn, M., Kendall, K., Mallon, C., Andrews, J., 2008. Steam reforming of biodiesel by-product to make renewable hydrogen. *Bioresource technology* 99(13), 5851-5858.
- Sokka, L., Lehtoranta, S., Nissinen, A., Melanen, M., 2011. Analyzing the Environmental Benefits of Industrial Symbiosis: Life Cycle Assessment Applied to a Finnish Forest Industry Complex. *Journal of Industrial Ecology* 15(1), 137-155.
- SP, 2013. Bioraffinaderier för ett grönt Sverige – en strategisk forsknings- och innovationsagenda för utveckling av branschöverskridande bioraffinaderi-koncept . SP Sveriges Tekniska Forskningsinstitut.
- Srinivasan, S., 2009. The food v. fuel debate: A nuanced view of incentive structures. *Renewable Energy* 34(4), 950-954.
- Srirangan, K., Akawi, L., Moo-Young, M., Chou, C.P., 2012. Towards sustainable production of clean energy carriers from biomass resources. *Applied Energy* 100, 172-186.
- Sun, F., Chen, H., 2008. Organosolv pretreatment by crude glycerol from oleochemicals industry for enzymatic hydrolysis of wheat straw. *Bioresource technology* 99(13), 5474-5479.
- Sun, J., Fujita, S.-., Arai, M., 2005. Development in the green synthesis of cyclic carbonate from carbon dioxide using ionic liquids. *Journal of Organometallic Chemistry* 690(15), 3490-3497.
- Svensk Biogas AB, 2013. Available At: <www.svenskbiogas.se>. Accessed: August 25, 2013.
- Taheripour, F., Hertel, T.W., Tyner, W.E., Beckman, J.F., Birur, D.K., 2010. Biofuels and their by-products: Global economic and environmental implications. *Biomass and Bioenergy* In Press, Corrected Proof

- Talebna, F., Karakashev, D., Angelidaki, I., 2010. Production of bioethanol from wheat straw: An overview on pretreatment, hydrolysis and fermentation. *Bioresource technology* 101(13), 4744-4753.
- Taylor, G., 2008. Biofuels and the biorefinery concept. *Energy Policy* 36(12), 4406-4409.
- Tilman, D., Socolow, R., Foley, J.A., Hill, J., Larson, E., Lynd, L., Pacala, S., Reilly, J., Searchinger, T., Somerville, C., Williams, R., 2009. Beneficial biofuels - The food, energy, and environment trilemma. *Science* 325(5938), 270-271.
- Timilsina, G.R., Shrestha, A., 2011. How much hope should we have for biofuels? *Energy* 36(4), 2055-2069.
- Tripathi, M.K., Mishra, A.S., 2007. Glucosinolates in animal nutrition: A review. *Animal Feed Science and Technology* 132(1-2), 1-27.
- USA Law, 2007. Energy Independence and Security Act 2007. Energy Independence and Security Act of 2007.
- Vasudevan, P.T., Briggs, M., 2008. Biodiesel production - Current state of the art and challenges. *Journal of Industrial Microbiology and Biotechnology* 35(5), 421-430.
- Vlysidis, A., Binns, M., Webb, C., Theodoropoulos, C., 2011. A techno-economic analysis of biodiesel biorefineries: Assessment of integrated designs for the co-production of fuels and chemicals. *Energy* 36(8), 4671-4683.
- Vuholm, S., Arildsen Jakobsen, L.M., Vejrum Sørensen, K., Kehlet, U., Raben, A., Kristensen, M., 2014. Appetite and food intake after consumption of sausages with 10% fat and added wheat or rye bran. *Appetite* 73(0), 205-211.
- Wang, L., Littlewood, J., Murphy, R.J., 2013. Environmental sustainability of bioethanol production from wheat straw in the UK. *Renewable and Sustainable Energy Reviews* 28(0), 715-725.
- Wang, T., Lu, S., 2013. Production of xylooligosaccharide from wheat bran by microwave assisted enzymatic hydrolysis. *Food Chemistry* 138(2-3), 1531-1535.
- Wetterlund, E., 2012. System studies of forest-based biomass gasification. Linköping University, Energy Systems.
- Wheat Foods Council, 2013. Available At: <http://www.wheatfoods.org/sites/default/files/atachments/kernel-wheat-how-flour-milled.pdf>.
- Xu, Y., Isom, L., Hanna, M.A., 2010. Adding value to carbon dioxide from ethanol fermentations. *Bioresource technology* 101(10), 3311-3319.
- Yazdani, S.S., Gonzalez, R., 2007. Anaerobic fermentation of glycerol: a path to economic viability for the biofuels industry. *Current opinion in biotechnology* 18(3), 213-219.
- Zeng, X., Danquah, M.K., Chen, X.D., Lu, Y., 2011. Microalgae bioengineering: From CO₂ fixation to biofuel production. *Renewable and Sustainable Energy Reviews* 15(6), 3252-3260.