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Lifecycle Analysis of a *n*-caproate production system on an industrial scale

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I. Introduction

The corn to ethanol industry has successfully proven to be a source of fuels towards reducing the use of fossil fuels and contributing to energy security; however, a limit of 15 billion gallons of corn based ethanol has already been reached and the US Government no longer encourages additional corn-based biofuels [1].According to the U.S. Renewable Fuel Standards mandate [1], additional biofuel production should be coming from cellulosic and advanced biofuels, with the goal of having 21 billion gallons of nonconventional biofuels by 2022. This mandate, along with the expiration of the blenders subsidy of 45 cents per gallon in December 2011[2] have placed corn based ethanol producers in a difficult situation where growth and even subsistence will depend on the producers ability to diversify their production and sell value added products otherthan ethanol.

In this study an alternative production pathway is presented to synthesize *n*-caproate from corn using a Dry Mill Corn to Ethanol model based on an actual corn to ethanol plant built in 2005. The proposed pathway requires a diversion of the process at the “Corn Beer” stage towards a secondary reactor where *n*-caproate is produced.The model is based in the Angenent Lab experiment where a sequencing batch reactor with pH 5.5 and temperature of 30°C was fed with corn beer at rates of 8.03 g COD/L/Day [5,9] to elongate carboxylic acid chains and produce *n*–caproate at rates up to 2.1 g per liter of reactor daily. The *n*-caproate is then removed from the fermentation liquor using a membrane pertraction system driven by pH gradient.This product can be used in the pharmaceutical industry, as a feedstock with probiotic properties [10]or as a biofuel precursor to produce *n*-hexanol or *n*-butanol.

The specific objective of this study is to determine whether the *n*–caproate pathway is energetically favorable, to reach this goal a Life Cycle Assessment (LCA) process is completed to calculate the net energy balance (NEB) ratio of the process and compare it to the corn to ethanol traditional pathway. During this process all the energy inputs of the system are taken into account and are compared with the energy density of the final products. In this particular case the boundary of the system will be drawn around the plant considering all the energetic inputs of the raw materials compared to the energetic value of the products and co products.

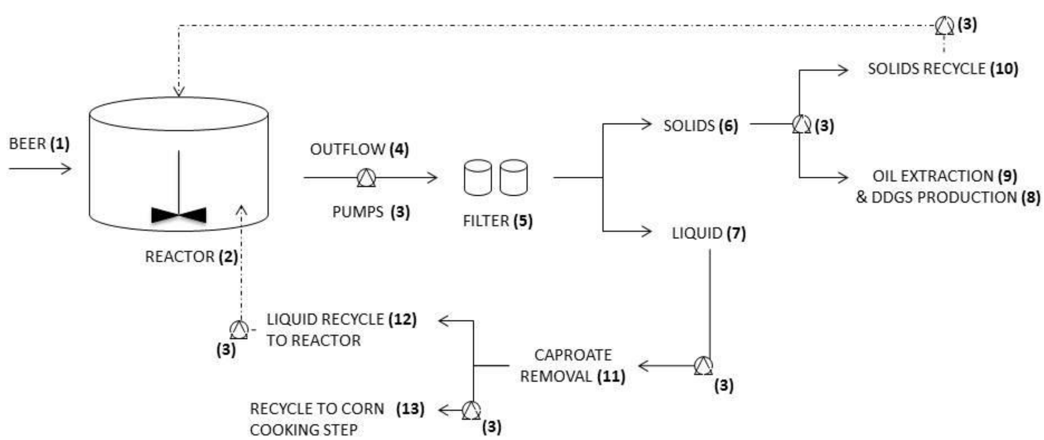
II. Integrating the Carboxylic Platform in the Corn to Ethanol Plants

The carboxylic platform refers to fermentation of ethanol and other intermediates as acetate and *n*-butyrate so as to produce both short and medium-chain carboxylates through a reversed β-oxidation pathway. The conditions of the secondary reactor have to be anaerobic, 30°C and pH must be preserved at 5.5 for microorganisms to grow and elongate ethanol and/or with acetate molecules to produce medium chain carboxylic acids as *n*–caproate [3].

One of the stages in the corn to ethanol industry is the corn beer production step that precedes the distillation process, at this point [4] the corn kernels have been grinded, cooked, and fermented to produce corn beer with 14 – 15% ethanol. The proposed pathway considers diverting the corn beer to a secondary completely stirred tank reactor in anaerobic conditions with a 10-day retention time. During this period a fraction of the solids will break down to produce acetate, which along with the ethanol molecules will elongate to produce *n*–caproate.

As shown in Figure 1, the *n*–caproate production facility should be built using the same base process of the ethanol plants to corn beer ready on site to feed the carboxylic reactor where chain elongation will take place. The following scheme shows the flow chart of the system with each of the critical components used.

Figure 1. Schematic of the n-caproate production system that will be integrated in an existing corn to ethanol plant.



1. Beer Inflow: The design considers an inflow of 650 gpm of beer coming from the beer well; this figure is typical of a 55 million gallon Corn to ethanol Dry Milling Plant. The beer contains 15% ethanol, with other co-products; such as corn fiber, proteins, oils, partially hydrolyzed carbohydrates, and yeast cells from the previous fermentation step.
2. Two stainless-steel completely stirred tank reactors (CSTR) totaling 10,000,000 gallons are used in this design to reach a 10 day hydraulic retention time of the beer in the carboxylic reactors. Each reactor will have a permanent stirring system, an acid-base control system to keep the pH at 5.5, and a temperature control. The mixed-culture anaerobic reactors contain bacterial communities, including the species *Clostridium kluyveri*, which will convert ethanol and acetate into *n*–caproate.
3. Pumps in the system are given in chronological order in the table below. Given that the design has two reactors, the overall design also considers two sets of all of these pumps.
4. Outflow: The outflow of the reactor considers removing a daily outflow equal to 1.5 times the volume of each reactor, of which 93% is recycled back to the reactor and the other 7% goes out of the cycle to produce DDGS and oil (solid phase) and to be used in the initial corn cooking steps (liquid phase).
5. The filter used to separate the solid phase from the liquid phase in the outflow is a Centrifugal Discharge Filter that separates the solids from the liquids efficiently.
6. Solid phase recovery: The centrifugal filter will separate the solids in the reactor liquor from the liquids. Part of the solids will recycled back to the reactor for further breakdown and the liquid phase will be sent to the *n*-caproate pertraction system.
7. The outflow liquid of the filter will carry the soluble *n*–caproate which will be passed through a membrane pertraction system where *n*–caproate will be removed.
8. Oil extraction: The solids going out of the system will be oil extracted with a solvent to sell this product to the biodiesel industry.
9. DDGS Production: Once the oils have been removed from the solid phase, the resulting product can be sold as Wet Distillers Grain or as Dry Distillers Grain, just as it's currently being done at the Corn to Ethanol Dry Milling plants.
10. Solid recycle: Given the high recycling rate in the system, most of the solids removed by the filter will return to the reactor to continue the breakdown process and donate carbohydrates and intermediate products to produce *n*–caproate and feed the microorganisms.

11. *n*–caproate Removal: Removal of *n*–caproate has to be permanent and efficient to avoid excessive concentrations of the product that may be toxic to bacteria diverting the process to different microbial pathways. To remove the *n*–caproate from the liquid phase, a membrane pertraction system driven by a pH gradient is installed on site. The membranes remove the *n*–caproate using a mineral oil as interface without the need of additional energy inputs other than pumping liquids through the system. The surface of membrane required to remove all the *n*–caproate of the liquid has to be approximately 18,500 m^2 considering the same extraction rates achieved in the lab with membrane Liquicel modules. The membrane surface required to make this process feasible remains to be the main obstacle of the n- *n*–caproate production pathway, this issue will be addressed in the discussion chapter.
12. Liquid Recycle to Reactor: After the *n*–caproate has been removed from the filtered reactor liquor, 93% of the liquid goes back to the reactor where other carboxylic chains are to be elongated to produce *n*–caproate.
13. Liquid recycle to corn cooking step: 7% of the liquid removed from the reactor is going to be taken away from the system, cleaned up by an anaerobic digestion system, and reused at the very beginning of the beer production process.

III. Lifecycle Assessment Methods and Tools

LCA processes are systems to determine the environmental impacts of a certain product or service “from cradle to grave”, considering the impact of all the production stages and the impact involved in the production of all materials used in the process. In this study the LCA approach will be used to determine the fossil fuel energy required to producing one unit of ethanol and one unit of *n*–caproate, and compare them to their corresponding energetic value using the NEB ratio shown in equation [12}.

$$NEB_{ratio} = \frac{Energy\ density\ of\ the\ product}{Energy\ required\ to\ produce\ one\ unit\ of\ product}$$

Depending on the results of the LCA process, the following scenarios exist:

- $NEB_{RATIO} < 1$: The fossil energy required to produce one unit of fuel is higher than the energy in the fuel; therefore from an energetic point of view it would be more convenient to just use the primary fossil fuel source instead of producing a secondary fuel.
- $NEB_{RATIO} = 1$: The fossil energy required to produce one unit of fuel is the same than the energy in the fuel, in this case from an energetic perspective there is no difference to just use the fossil fuel instead of producing a secondary fuel.
- $NEB_{RATIO} > 1$: The fossil energy required to produce one unit of fuel is lower than the energy in the fuel produced; from an energetic perspective this makes sense because at the end of the process there is an energy gain.

The boundary of the process will be considered around the processing plant, this means that all the focus will be given to the processes going inside the plant; however, the fossil energy load embedded in each of the inputs coming into the plant will be considered to determine the total fossil energy consumption per unit of *n*–caproate produced. An LCA process can be very complex because of the multiple processes and materials involved in the production of each and every material used in the main production process; therefore, one of the most critical steps in a LCA process is determining the boundaries of the system. This is step will ensure that the results will address the question to be asked without over expanding the system to other productive systems, with the risk of bringing in higher levels of uncertainty.

According to Wang [6,12], there are five different alternatives to account the value of co-products during a LCA process involving more than just one product; this is a very common situation in the biofuel industry where animal feed is usually a major co-product both in terms of mass balance and economic relevance.

i. The mass based method[6,12]: The allocation of energy and emissions during the biofuel production process is assigned to each product and co-product on a mass basis. The assumption underlying this method is that the energy is distributed equally in products and co-products as a function of their mass.

ii. The energy content based method[6,12]: The allocation of energy and emissions is distributed between products and co-products as a function of their energetic content. This method is very successful when all the products and co-products are used as fuels.

iii. The market based value method[6,12]: The distribution of energy use and emissions is made accordingly to expected revenues coming from each of the products and co-products. “This method assumes that activities and decisions are driven by economics and thus burdens should be disbursed according to economic benefits” [6].

iv. The process purpose based method[6,12]: This method allocates energy and emission burdens depending on the energy and emissions associated with the production and end use of each product and co-product. This method requires to determine the exact amount of energy and/or emissions associated to each product; this method is not feasible when products and co-products share one or more production steps (e.g. both ethanol and DDGS both come from corn and share the same production steps up to the “corn beer” stage)

v. The displacement method [6,12]: In this case, substitutes for the co-products produced are identified and energetic costs and emissions burdens are determined for them. This method subtracts the energy of the corresponding displaced substitute products from the biofuel production process in order to give credit for those co-products.

In this study, the displacement method will be used to account for the value of co products DDGS, Corn Oil and Liquefied CO_2 both for the corn to ethanol and corn to *n*–caproate process. This method was chosen because it is the only method that considers having different product and co products with different end uses and values sharing most of the biofuel production pathway.

- DDGS Substitution: According to the nutritional composition of DDGS, a nutritionally similar mix of feedstocks would be rapeseed meal and rapeseeds on a 4.78:1 ratio.

Table 1. Nutritional composition of DDGS and Alternative Feedstocks

		DDGS WNY [A]	Rapeseed Meal	Rapeseed
Dry Matter	%	88.3	90.3	89.9
Crude Protein	% db.	30.8	37.8	20.5
Net Energy Lactation	Mcal/Kg db.	2.1	1.76	3.52
Acid Detergent Fiber	% db.	32.0	29.8	17.5
Neutral Detergent Fiber	% db.	13.4	20.5	11.6

SOURCES: WNY Ethanol Plant [A], NRC Nutritional Requirements of Dairy Cattle

Table 2. DDGS Equivalency with Alternative Feedstocks

		1,000 Kg DDGS	761 Kg Rapeseed Meal	159 Kg Rapeseed	**910 Kg Total**
Crude Protein	Kg	**272**	260	29	**289**
Net Energy Lactation	Mcal	**1,813**	1,209	504	**1,713**
Acid Detergent Fiber	Kg	**320**	205	25	**230**
Neutral Detergent Fiber	Kg	**134**	141	17	**157**

This means that the energy credit given per ton of DDGS produced will be equivalent to the energy required to produce 761 Kg of Rapeseed Meal and 159 Kg of Rapeseed.

- Corn Oil Substitution: Soybean oil is considered a similar substrate than Corn Oil for Biodiesel production processes; therefore, the energy credit given to the Corn Oil will be equivalent to the energy required to produce the similar amount of Soybean Oil.
- Liquefied Carbon Dioxide Substitution: Carbon dioxide can also be recovered from processes such as steam reforming to produce ammonia; therefore the energetic cost involved in the recovery of 1 ton of CO2 from the ammonia production process will be given as credit per ton of CO2 recovered in the ethanol plant.

IV. Results

The results displayed in the table below represent the fossil energy consumption in the corn to *n*–caproate model in Megajoules per kilogram of *n*–caproate compared to the ethanol pathway.

Table 3. Fossil Energy consumption in ethanol and *n*-caproate pathways

	Ethanol		n-caproate		
	MJ/Kg	%	MJ/Kg	%	
Corn	11.44	46.9%	15.60	65.5%	
Natural Gas	11.07	45.4%	7.23	30.4%	
Gasoline	1.19	4.9%	-	0.0%	
Urea	0.40	1.6%	0.55	2.3%	
Enzymes	0.15	0.6%	0.15	0.6%	
Sodium Hydroxide	0.08	0.3%	0.21	0.9%	
Plant Infrastructure	0.03	0.1%	0.04	0.2%	
Ammonia	0.02	0.1%	0.03	0.1%	
Electricity - Hydropower	0.01	0.1%	0.02	0.1%	
Phosphoric Acid	2E-04	0.0%	3E-04	0.0%	
Sulphuric Acid	1E-04	0.0%	2E-04	0.0%	
Total	**24.39**	**100.0%**	**23.82**	**100.0%**	
Carbon Dioxide	-6.93	74.1%	-9.45	85.0%	*CO_2 Credit*
Natural Gas	-	0.0%	-0.49	4.4%	*CH_4 Credit*
Rape seed meal	-0.33	3.5%	-0.16	1.5%	*DDGS Credit*
Rape seed	-1.90	20.3%	-0.89	8.0%	*DDGS Credit*
Soybean Oil	-0.19	2.1%	-0.12	1.1%	*Corn Oil Credit*
Total	**-9.36**	**100.0%**	**-11.11**	**100.0%**	

	MJ/Kg Ethanol	MJ/Kg n-caproate
Total Energetic Cost	15.03	12.70
Energy Density	29.70	30.06
Net energy Balance	1.98	2.37

According to the handbook of chemistry and physics[16] the heat of combustion of *n*–caproate at 25° C is 30.06 MJ/Kg and the heat of combustion of ethanol is 29.7 MJ/Kg. It is important to consider that this model has not yet taken into account the energetic load associated to the membranes required in the *n*–caproate pertraction system.

If the current extraction rates observed in the lab were used for this analysis, 1.93 additional MJ per kilogram of *n*–caproate should be considered as the membrane energetic burden (see appendix # 2). The NEB ratio in this case would be 2.05 as shown in table 4.

Table 4. Net Energy Balance ratio at current membrane extraction rates

	MJ/Kg Ethanol	MJ/Kg n-caproate
Total Energetic Cost	15.03	14.63
Energy Density	29.70	30.06
Net energy Balance	1.98	2.05

Looking at the NEB ratio of ethanol and *n*–caproate it seems as they were fairly similar; however, it must be taken into account that this is a comparison between an alcohol and a carboxylate and they have different combustion behavior. To avoid misleading comparisons between ethanol and *n*–caproate, calculations are made to simulate the conversion of later to *n*-hexanol assuming 10% extra energy fossil fuel energy consumption associated to this transformation. The NEB ratio comparison between ethanol and *n-hexanol* without considering the fossil fuel expenses associated to membranes would look as it follows.

Table 5. Net Energy Balance ratio comparison between ethanol and *n*-hexanol pathways

	MJ/Kg Ethanol	MJ/Kg Hexanol
Total Energetic Cost	15.03	17.01
Energy Density	29.70	39.10
Net energy Balance	1.98	2.30
Yearly Production Kg	167,786,000	123,076,606
Gross Energy MJ	4,983,244,200	4,812,295,295
Net Energy MJ	2,461,013,148	2,955,962,382

The gross energy recovered from an ethanol plant scenario compared to a *n*-hexanol plant is 3% higher; however, after deducting the fossil energy that has been invest in each system we get a yearly net energy production 20% higher for the *n-hexanol* production scenario.

V. Discussion

Clearly, a large dependency of fossil fuel energetic costs to produce corn exists, representing 46.9% of the ethanol energetic cost and 65.5% of the *n*–caproate energetic cost. The highest dependence in the case of the *n*–caproate is a consequence of a lower production volume. In this sense its important to consider that the energetic burden associated to corn is calculated as a function of the corn yield in the fields, and therefore farmers achieving better yields will produce corn with less energetic burden than average yield corn producers. This calculation could be more precise if the actual yields of the farms providing the corn were considered, along with their average artificial irrigation and tillage practices. In addition, the natural gas has a very high impact on the energetic load of both systems; however, there is a big difference in natural gas consumption between the ethanol and *n*–caproate pathways given by the absence of a distillation tower and smaller amount of DDGS produced in the *n*–caproate pathway. In both scenarios corn energetic load and natural gas represent over more than 90% of the total energetic burden of the system.

Carbon dioxide credit given for the production of liquefied CO_2 in both systems is considerable, accounting for 74% and 85% of the total energetic credits in the ethanol and *n*–caproate pathways, respectively. If carbon dioxide coming from fermentation systems as corn beer production was not available it would need to be recovered either from steam reformation processes that are very energy demanding or cleaning up CO_2 from selected combustion processes, which is also energy demanding. Given the large availability of liquefied CO_2 in the US coming from ethanol plants it is unlikely that these alternative industrial processes end up supplying the CO_2 demand.

Another alternative to make these results more accurate would be to refine the DDGS substitution method using a wider variety of feedstocks. If a mixture of 19% Corn Grains, 25% Soy Meal (with 44% Crude Protein), 51% Wheat Bran, and 5% of Rapeseed feedstocks were used the nutritional value would be much closer to actual DDGS composition than the Rapeseed Meal and Rapeseed used method; however, lifecycle information on most of these feedstocks is currently unavailable.

VI. Conclusions

The NEB ratio calculated for the *n*–caproate pathway is 2.37 based on an existing ethanol plant production parameters and the *n*–caproate experimental results reported by Agler et al. in 2012 [9]. This NEB ratio does not consider the energetic load associated to the membranes required in the pertraction process. For every unit of energy that goes into the *n*-caproate pathway there is an energy gain of 1.37 units. If the membrane energetic load was considered at the rates currently observed in the experiment [9], the NEB ratio would drop to 2.05. The current extraction methodology has not been optimized yet and data observed in similar processes in industry state clearly that there is a big gap between the potential extraction rates and the rates observed experimentally.

The *n*-caproate production technology proves to be a successful alternative pathway in the corn to ethanol industry. To compare the NEB ratio between *n*-caproate to ethanol an additional transformation has to be done from *n*–caproate to *n*-hexanol, otherwise the comparison between the energetic performance of an alcohol versus a carboxylate can be misleading. In this study we assume that an extra 10% of fossil fuel energy is required to transform *n*-caproate into *n*-hexanol to make a comprehensive comparison between the NEB ratio of ethanol and *n*-hexanol.

If the *n*-caproate were converted to *n*-hexanol, the NEB ratio without considering membranes is 2.59 and using membranes at currently reported extraction rates is 2.3. This means that for every unit of fossil fuel invested into the system, between 1.3 and 1.59 additional units of energy are harvested in the form of *n*-hexanol.

One of the major drawbacks of switching from ethanol to *n*-hexanol production is the volume reduction associated to producing *n*-caproate instead of ethanol. According to the data used in this study [9] a corn to ethanol plant will only produce 73% of the previously produced kilograms of ethanol in the form of *n*-caproate. There is also the fact that DDGS and Oil production decrease in 66% and 53% respectively, this is something that must be analyzed from a financial point of view to determine whether the higher price for *n*-hexanol makes up for the lower income associated to co product sales.

Membrane efficiency improvement should be one of the main objectives of future research initiatives. Even when the energetic load associated with having a rate of extraction similar to the one observed in the lab does not compromise a favorable NEB ratio with regards to the ethanol production pathway it is important to recognize that such large surface of membrane is not available on the market and cannot be successfully installed in an industrial facility. Potentially alternative systems, such as pervaporation, may be used to improve the extraction rates using smaller membrane surfaces [22].

Another big challenge associated to the *n*-caproate pathway is the dimensions of the carboxylic reactor needed to reach a hydraulic retention time of 10 days of the corn beer. This represents a major capital cost for the system that may be reduced exploring the possibility of feeding the reactor only with the liquid phase of the corn beer to reduce the retention time required to convert the ethanol into *n*-caproate. Separating the solids contained in the beer before diverting it to a carboxylic reactor would preserve the same amount of DDGS produced by the plant assuring a large share of income from this co product. However, another source of organic carbon should be provided to replace the organic compounds the solids provide for chain elongation

Market opportunities for *n*-caproate in the form of caproic acid should also be revised to assess the risk of over supplying the market causing a price reduction. In this sense alternative uses for the product as animal feed probiotic[23] or the conversion of caproic acid to *n-hexanol*/butanol[24] would allow the allocation of this product in the commodity markets where volumes are not restrictive.

VII. Appendix 1 –LCA Key Assumptions

1. Infrastructure: To perform this study, it has been assumed that the energetic load corresponding to the infrastructure and operation of a *n*-caproate plant right after the corn beer stage is equivalent to the energetic load of having the post corn beer ethanol plants have. This means that all the infrastructural load and energy used in an ethanol plant after the corn beer stage isassumed to be the same than the infrastructural load and energy use in a *n*-caproate plant right after the corn beer stage.The base construction materials of the ethanol plant and their energetic load have been obtained from Sima Pro database [14].Data available comes from an ethanol plant with an annual capacity of 90,000 tons and a life time of 20 years in the USA, this data has been linearly extrapolated to reach the desired plant size of 167,786 tons/yr. or 56,178,205 gal/yr.
2. Membranes: The efficiency of the pertraction system remains to be one of the major challenges this alternative pathway faces.The extraction rates achieved in previous experiences [9] have been 27.8 g *n*-caproate Day $^{-1}$ using two membrane extraction modules of 8.1 m^2 each.The membrane surface required to remove *n*-caproate in an industrial scale plant would be unrealistic at these extraction rates. However, theextraction systems have not been optimized yet in the previous experiments [9], and the experience on similar extraction systems in other industries reveals an optimistic solution to this challenge. Given the uncertainty associated with the energetic load of the membranes in this LCA study, no energetic load will be associated to the *n*-caproate pathway; instead calculations will be made to determine what would be the maximum energetic load associated to the membrane extraction system to reach the same NEB ratio than the Corn to Ethanol industry. A detailed model on how to calculate the impact of the membranes on the overall *n*-caproate production can be found on appendix # 2.
3. DDGS: Given that DDGS has no value as a direct fuel source, the substitution method was used to determine the energy credit. The nutritional characteristics of the DDGS in terms of crude protein, energy and fiber are most similar to a mixture of 82.7% Rapeseed Meal and 17.3% Rapeseed grains; however given the higher nutritional value of these alternative feedstocks only 91% of the total weight of DDGS at 88.3% dry matter should be replaced by this rapeseed mixture.
4. Liquefied Carbon Dioxide: The energy credit calculated for this co product was calculated as a function of the energy required to produce carbon dioxide using an alternative process.In this case the production process of ammonia and CO_2 was considered using the Ecoinvent process database

[14]using the model for extraction carbon dioxide out of waste gas streams from different production processes with a 15-20% monoethanolamine solution followed by a purification and a liquefaction step, using each electricity as energy source in Switzerland,data are assumed to be valuable for European conditions[14].

5. Corn Oil: The energy credit given by Corn oil production corresponds to the energy required to produce the same amount of soybean oil. Soy beans used in the process come from an US exploitation system with an average yield of 2641 kg/ha with 11% moisture. The oil extraction process is done using hexane as solvent. The allocation of inputs and outputs are allocated 28% to soya oil and 72% to soya scrap[14].
6. Enzymes – Yeast – Antibiotics:The energetic load coming from the production of enzymes, yeast and antibiotics will be considered to be the same for all these products given their common production processes through fermentation systems. An average energetic burden of 60 MJ/Kg of product is considered, this is derived from an Enzyme LCA studied done by Nielsen, Oxenboll and Wenzel in 2007[11].
7. Agricultural Corn Production: The energetic burden of corn production in terms of fossil fuel energy inputs is calculated using the US corn production case. An averageyield of 9315 kg/ha with 14% moisture is considered[14].
8. Natural Gas:The fossil energy impact coming from the use of natural gas comes both from the energy contained in the natural gas itself along with a share of the infrastructural and operational loads associated with transport and processing. Calculated using data from Germany, assumed to be equivalent to the US natural gas industry[14].
9. Electrical Power: The electrical power used in this study is coming from a Hydropowerplant model coming from the operation of Brazilian dams; it includes the area occupied; a preliminary estimation of greenhouse gas emissions out of the water reservoir based on actual literature; lubricant oil; volume of the reservoir; mass of water passing through the turbines. The lifetime of the plant is assumed to be 150 years for the structural part and 80 years for the turbines[14]. Is important to clarify that only the fossil fuel energy that has been used for the plant construction, materials and transmission lines will be considered as fossil energy load for hydropower. Given the large amount of power a hydro plant produces during its lifetime, the fossil fuel energy load is very low compared to other thermal sources of power.

10. Denaturant: The denaturant used in the ethanol production process is gasoline a rates of 25 ml per gallon of ethanol. The energetic load of the gasoline is calculated considering all flows of materials and energy due to the throughput of 1kg crude oil in the refinery[14].

11. Acid and Base Consumption: Up to the corn beer stage the consumption of sodium hydroxide and sulfamic acid are 1,848,657 lb./yr. and 20,488 lb./yr. respectively for a 56,000,000 gal/yr. ethanol plant. In the *n*-caproate production system the base consumption is considerably higher because of the large volumes of stripping solution required in the pertraction system and the acid required to reduce the pH in the *n*-caproate enriched stripped solution to achieve phase separation. In this study a 90% recovery efficiency has been considered both for bases and acids used in the *n*-caproate extraction process, totaling a consumption of 1,729,116 lb. NaOH/yr. and 3,767 lb. Sulfamic Acid/yr.

12. Conversion rates used in the model:

Table 6. Conversion table used in the LCA model

	Corn to Ethanol Model	Corn to n-caproate Model
Kg of Corn per L of Ethanol	2.3	-
Kg of Corn per Kg of n-caproate	-	4.0
Kg of Corn per Kg of DDGS	3.1	9.1
Kg of Corn per L of Corn Oil	110.6	238.9
Kg of Corn per SCF of Methane Methane	-	10.7
Kg of Corn per Kg of Liquefied CO_2	4.6	4.6

VIII. Appendix # 2 – Membrane energetic load

Model for calculation of fossil fuel energy associated to polypropylene membrane production

A. Parameters

1.	Polypropylene fossil energy load	79	MJ/Kg	[17,19]
2.	Polypropylene density	0.92	g/cm^3	[18]
3.	Membrane Porosity	58.5%		[20]
4.	Membrane Thickness	100	micron	
5.	Membrane lifespan	2.5	years	[21]

B. Laboratory Yields

6.	Membrane surface per side	8.1	m^2 membrane
7.	Extraction rate	27.8	g *n*-caproate/day
8.	Extraction rate	3.4	g *n*-caproate/day· m^2

C. Industrial *n*-caproate extraction requirements

9.	Desired extraction	337,196,181	g *n*-caproate/day
10.	Surface membrane needed	98,247,808	m^2 membrane
11.	Volume of membrane needed	9,284,780,808	cm^3 membrane/side
12.	Total volume of membrane needed	19,649,561,616	cm^3 membrane
13.	Total weight of membrane needed	7,502,203	Kg polypropylene

D. Impact calculation per unit of *n*-caproate

14.	Fossil energy load	592,674,007	MJ/membrane set
15.	Yearly fossil fuel load	237,069,603	MJ/year
16.	Yearly *n*-caproate production	123,076,606	Kg *n*-caproate/yr.
17.	Membrane load per kg *n*-caproate	1.93	MJ/Kg *n*-caproate

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