MATERIAL AND ENERGY FLOWS IN THE PRODUCTION OF MACRO AND MICRONUTRIENTS, BUFFERS, AND CHEMICALS USED IN BIOCHEMICAL PROCESSES FOR THE PRODUCTION OF FUELS AND CHEMICALS FROM BIOMASS

Felix Adom, Jennifer B. Dunn

Energy Systems Division

Argonne National Laboratory

September 30th, 2015

TABLE OF CONTENT

Tables

1. INTRODUCTION

Argonne National Laboratory's Greenhouse gases, Regulated Emissions, and Energy use in Transportation (GREET) model contains a bioproducts module that estimates the energy consumption and air emissions, including greenhouse gas (GHG) emissions of commercially-relevant bioproducts (Dunn et al. 2014). In the 2014 GREET release, eight bioproducts (propylene glycol, acrylic acid, 3-hydroxypropanoinc acid, succinic acid, polyethylene, isobutanol, 1,4-butanediol and 1,3-propanediol) produced from either algal glycerol or corn stover-derived sugars were selected for inclusion in the bioproduct module.

The bioproduct module has been expanded to incorporate two additional bioproducts (L-lactic acid and ethyl lactate) for the 2015 GREET release (Dunn et al., 2015). In the expansion process, it became necessary to include material and energy flows associated with producing some key nutrients (macro and micro), buffers, and chemicals used in fermentation media. We therefore assembled the life cycle inventory data (material and energy flows) for these compounds and incorporated them into the module. In this memo, we document these data, their sources, and key assumptions we adopted.

2. DESCRIPTION OF THE MATERIAL AND ENERGY FLOW DATA DEVELOPMENT PROCESS

In this section of the memo, we describe in detail the nutrients included in the GREET bioproducts module. Additionally, we briefly describe the production processes of these nutrients, primary data sources and key assumptions used to fill data gaps. Finally, we report the material and energy flow intensities incorporated into the GREET model for each of these nutrients.

2.1 Macronutrients

Maintenance and enhancement of microbial cell performance requires the uptake and efficient utilization of nutrients. Macronutrients are a class of nutrients required in large amounts to support cell energy, growth and metabolism (Shuler and Kargi 2002). In this section, we describe the production of two important macronutrients, namely, yeast extract and magnesium sulfate monohydrate ($MgSO_4$. H_2O), which are often used as fermentation medium constituents.

2.1.1 Yeast extract

Apart from the inorganic nitrogen sources [e.g., $(NH_4)_2SO_4$), (NH_4Cl)], there are alternative organic nitrogen sources such as yeast extract and peptones, although these organic N sources can be relatively expensive. Produced from yeast via autolysis or hydrolysis process, yeast extract provides many nutrients including nitrogenous compounds, carbon, sulfur, trace nutrients, vitamin B complex and other vital growth factors essential for cell microbial growth (Sigma Aldrich 2015a).

Material and energy flows for the production of yeast extract were developed based on personal communication (Kim 2015) regarding a published LCA of pharmaceutical industry enzymes (Kim et al., 2009). These authors assumed that yeast extract was derived from spent yeast from ethanol fermentation process. It was not clear which of the yeast extract production processes [autolysis, plasmolysis or hydrolysis (Tanguler and Erten 2008)] was adopted in their study.

Energy consumption, air emissions, and other burdens were allocation were allocated between ethanol and the yeast extract.

2.1.2 Magnesium Sulfate Monohydrate (kieserite)

As a naturally occurring mineral in geologic marine salt deposits, kieserite is also chemically known as magnesium sulfate monohydrate ($MgSO_4 \cdot H_2O$) (Seeger et al. 2000). Kieserite is particularly useful in fermentation media because of its ability to provide soluble source of Mg and S (IPNI 2012). These essential macronutrients are needed in relatively large amounts to support cell functions during microbial growth. For example, magnesium acts as an enzyme cofactor, supporting enzyme activity (Shuler and Kargi 2002). We adopted energy consumed in the extraction, beneficiation and grinding of kieserite from Haglund (1999), despite these data being developed for kieserite production in Germany, because no data for domestic kieserite production were available.

2.1.3 Material and Energy Flow Data For Macronutrients

Material and energy flow data used in GREET for the macronutrients are summarized in Table 1. Approximately 25% of the mass share for the material input required for the production of ammonium sulfate is ammonia with the remainder (75%) being sulfuric acid. The dominant input requirement for yeast extract is energy (diesel) consumption, which is approximately 4 MMbtu/ton. Small amounts of alphaamylase and glucoamylase are reported as input because the yeast extract is produced as a co-product of corn ethanol production, which consumes these enzymes. Finally, Haglund (1999) reported 1.0 MMbtu of energy is required for the extraction, beneficiation and grinding of a ton of kieserite.

Table 1: Summary of Material and Energy Intensity Flows of Macronutrients

Total Energy : (MMbtu/Ton)	**Ammonium Sulfate** (Stoichiometry)	**Yeast Extract** (Kim 2015)	**Magnesium Sulfate (kieserite)** (Haglund 1999)

Natural gas			1.0
Diesel		4.0	
Mass Input : (Ton/Ton)			
Ammonia	0.26		
Citric acid	0.74		
Alphaamylase		0.0005	
Glucoamylase		0.0017	

2.2 Micronutrient

Compared to their consumption of macronutrients, microorganisms consume notably less micronutrient to support physiological functions. Inadequate micronutrient levels, however, could extend the cell lag phase and subsequently impact microorganism specific growth rate and yield (Shuler and Kargi 2002). $Cu^{2+,}Mn^{2+}$,Na^{+} and other trace elements are considered to be micronutrients. In this section, we report the energy and material flow for anhydrous copper (II) sulfate.

2.2.1 Anhydrous Copper (II) Sulfate [$CuSO_4$]

Anhydrous copper (II) sulfate salt has gray to white coloration with a rhombic crystalline structure and occurs naturally as mineral hydrocyanite. It has applications in fungicides, antifouling paints, and many other uses (Wayne Richardson 2000).

It can be produced from the reaction between copper metal and sulfuric acid (reaction 2) (Wayne Richardson 2000). We based the amounts of material consumed in producing copper sulfate on stoichiometry (reaction 2). Energy consumption for purification and recovery was excluded from the analysis because of lack of data.

$$Cu + 2\ H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O \text{ (Reaction 2)}$$

Since the reaction is exothermic, we assumed that no energy input is required for this reaction to proceed.

2.2.5 Material and Energy Flow Data for Micronutrient

In Table 2, we summarize the material and energy intensity of anhydrous copper (II) sulfate salt considered in GREET.

Table 2: Summary of Material and Energy Intensity Flows of Micronutrient

Total Energy : (MMbtu/ton)	**Copper (II) Sulfate** (Stoichiometry)
Natural gas Electricity Residual Oil	
Mass Input : (Ton/Ton)	
Copper	0.40
Sulfuric acid	1.2
Manganese (II) oxide	
Salt	
CoO	
HCl	

2.3 Buffers

Maintaining an optimum pH in the fermentation system is essential to support the physiological activities of microorganisms and also enhance the activities of biological enzymes. We developed life cycle inventory data for three buffers, ammonium citrate, sodium citrate and sodium acetate. We describe in detail how the inventory data was developed and assembled in GREET in the subsequent sections.

2.3.1 Ammonium Citrate [$(NH_4)_2C_6H_6O_7$]

Ammonium citrate [$(NH_4)_2C_6H_6O_7$], also known as diammonium 3-carboxy-3-hydroxypentanedioate, is a white crystalline powder used as an analytical reagent and buffer. It also has application in the pharmaceutical industry as a diuretic (Weston et al., 2000).

Ammonium citrate is produced via neutralization of citric acid with ammonia (Weston et al., 2000). The levels of material inputs consumed in the production of ammonium citrate were estimated using stoichiometry (Reaction 4). In the absence of data, energy consumed in product recovery was excluded.

$$3\ NH_3 + C_6H_6O_7 \rightarrow (NH_4)_2C_6H_6O_7 + H_2O \text{ (Reaction 4)}$$

2.3.2 Sodium Citrate [$NaH_2C_6H_6O_7$]

Sodium citrate is a sodium salt of citric acid with uses as a preservative and food additive. As a conjugate base of a weak acid, sodium citrate can act as a good buffer or acidity regulator for biochemical reaction systems to help maintain or stabilize pH of the system (Merza et al. 2012).

Sodium citrate is produced via neutralization reaction between citric acid [$C_6H_6O_7$] and sodium hydroxide [NaOH]. Reaction 4 was used to develop the material intensity of sodium citrate. Due to the exothermic nature of reaction 4, we assumed no energy input is required for this reactions to proceed.

$$3NaOH + C_6H_6O_7 \rightarrow NaH_2C_6H_6O_7 + 3H_2O \text{ (Reaction 4)}$$

2.3.3 Sodium Acetate [$C_2H_3O_2Na$]

Sodium acetate ($C_2H_3O_2Na$), or sodium ethanoate, is a sodium salt of acetic acid. Major industrial applications include use in leather tanning and as a polymerization retardant in plastic manufacturing (Sigma Aldrich 2015b). Additionally, sodium acetate is widely used as a buffer reagent in molecular biology application.

Sodium acetate is produced from the reaction between acetic acid and sodium hydroxide. Jungbluth (2008) characterized the mass and energy flows was associated with this process as part of an investigation of solar energy storage systems.

We summarize the material and energy flow intensities of all the buffers in the subsequent section.

2.3.4 Material and Energy Flow Data for Buffers

Material and energy flows for buffers considered in this study are summarized in Table 3.

Table 3: Summary of Material and Energy Intensity Flows of Buffers

Total Energy : (MMbtu/ton)	**Ammonium citrate** (Stoichiometry)	**Sodium citrate** (Stoichiometry)	**Sodium acetate** (Jungbluth 2008)
Natural gas			1.7
Electricity			1
Mass Input : (Ton/Ton)			
Ammonia	0.26		
Citric acid	0.82	0.85	
Sodium hydroxide		0.23	0.26
Acetic acid			0.76

2.4 Acetic acid

Acetic acid (CH_3COOH) is a colorless, corrosive organic compound with extensive industrial applications. For example, as a chemical solvent, it is used as a starting material for a number of compounds such as vinyl acetate monomer, acetic anhydride, terephthalic acid and esters. In fact the largest end use of acetic acid is in the synthesis of vinyl acetate monomer (Malveda and Funada 2010).

Major commercial production routes for acetic acid include methanol carbonylation, acetaldehyde oxidation, butane/naphtha oxidation, and methyl acetate carbonylation (Wagner and Staff 2000). However, acetic acid synthesis via methanol carbonylation remains dominant because about 80% of global production is by this processing route (Malveda and Funada 2010).

As a result, we report the material and energy flows for acetic acid produced via the methanol carbonylation process also referred to as the "Monsanto Process" in Table 4. In this process, carbon monoxide reacts with methanol under the influence of a metal catalyst such as rhodium complex at temperatures and pressures ranging from 150-200°C and 33-65 atm respectively (Wagner and Staff 2000; Franklin Associates 2011).

Table 4: Summary of Material and Energy Intensity Flows of Acetic Acid

Total Energy : (MMbtu/ton)	**Acetic Acid** (Franklin Associates 2011)
Natural Gas	12
Electricity	0.58
Mass Input : (Ton/Ton)	
Methanol	0.54

The energy consumption data required for the production of acetic acid (Table 4) accounts for energy requirement for the production of carbon monoxide (Franklin Associates 2011). Of the total energy usage, about 5% is attributable to electricity consumption with the remainder (95%) due to natural gas consumption.

3. CRADLE-TO-GATE LIFE CYCLE ANALYSIS RESULTS

To estimate the cradle-to-gate fossil energy consumption, and air emissions, including GHG emissions of the nutrients (micro and macro), buffer and acetic acid, the material energy flow data reported in section 2 were configured in the GREET model. By adopting current upstream GREET background data for energy sources (e.g., natural gas, electricity) and process inputs such as citric acid, sodium hydroxide among others, we were able to estimate the FEC and GHG emissions (Elgowainy et al. 2014; GREET 2014; Dunn et al. 2014).

In this section, we present the cradle-to-gate LCA results estimated using the GREET model.

3.1 LCA Results

Table 5 summarizes the FEC and GHG emissions results for all the chemical compounds considered in this study.

Within the macronutrients, we estimated yeast extract to be the most fossil and GHG intensive. Kieserite was on average four times less fossil energy and GHG intensive compared yeast extract. The primary drivers for yeast extract were the consumption of diesel (97%) and enzymes (3%). such as alpha-amylase and glucoamylase.

Table 5: Summary of Cradle-to-Gate LCA Results

Category	**Chemical Compound**	**FEC (MMbtu/ton)**	**GHG Emissions (kgCO_2e/kg)**
Macronutrient	Yeast Extract	5.0	0.44
	Magnesium Sulfate (kieserite)	1.2	0.10
Micronutrient	Copper (II) Sulfate	15	1.4
Buffer	Sodium acetate	33	1.4
	Ammonium citrate	21	1.9
	Sodium citrate	17	1.8
Acid	Acetic acid	29	0.61

Sodium acetate was estimated to be the most fossil energy intensive for the buffers. Ammonium citrate and sodium citrate were 1.6-2 times less fossil energy intensive compared to sodium acetate. The GHG emissions profile was slightly different. GHG emissions (1.8-1.9 kgCO_2e/kg) for ammonium citrate and sodium citrate were similar. On average, they were 24% higher than sodium acetate.

Finally, FEC and GHG emissions for acetic acid are were estimated to be 29 MMbtu/ton and 0.61 kgCO_2e/kg. Energy consumption dominated, contributing 70% of the FEC. Natural gas and electricity consumption contribution to FEC were 65% and 5%, respectively, with methanol consumption (30%) contributing to the remainder. The breakout of contributors to acetic acid cradle-to-gate GHG emissions is about the same as that of cradle-to-gate GHG emissions.

4. CONCLUSIONS AND FUTURE WORK

We have developed life cycle inventory data for commonly used macronutrients, micronutrients and buffers in addition to one chemical compound (acetic acid) in GREET

Overall, data availability was a major challenge in the development of the life cycle inventory of these chemical compounds. In the absence of publicly available data, reasonable assumptions have been adopted to generate the material flows and also fill data gaps.

In the future, we will examine which of these nutrients are consumed in significant amounts in processes to produce biofuels and biochemicals and therefore should be prioritized for improvement. One technique we could use to improve data is to request industrial data or to use data obtained from permits of industrial facilities. Alternatively, we could develop a process simulation for the production of key nutrients or buffers in Aspen Plus. Finally, we are also interested in the water intensity of nutrient production, which we did not investigate at this time.

5. REFERENCES

Butts, David, and David R. Bush. 2000. “Sodium Sulfates and Sulfides.” In *Kirk-Othmer Encyclopedia of Chemical Technology*. John Wiley & Sons, Inc. http://onlinelibrary.wiley.com/doi/10.1002/0471238961.1915040902212020.a01.pub3/abstract.

Dai, Qiang. 2014. “Life Cycle Assessment of Natural Gas Utilization in Light-Duty Passenger Vehicles.” http://deepblue.lib.umich.edu/handle/2027.42/107285.

Donaldson, John Dallas, and Detmar Beyersmann. 2000. “Cobalt and Cobalt Compounds.” In *Ullmann’s Encyclopedia of Industrial Chemistry*. Wiley-VCH Verlag GmbH & Co. KGaA. http://onlinelibrary.wiley.com/doi/10.1002/14356007.a07_281.pub2/abstract.

Dunn, Jennifer, Felix Adom, Jeongwoo Han, Norm Sather, and Seth Snyder. 2015. “Life-Cycle of Bioproducts and Their Conventional Counterparts in GREET.” Technical Report ANL/ESD-14/9 Rev. Argonne National Laboratory.

Elgowainy, Amgad, Jeongwoo Han, Hao Cai, Michael Wang, Grant S. Forman, and Vincent B. DiVita. 2014. “Energy Efficiency and Greenhouse Gas Emission Intensity of Petroleum Products at U.S. Refineries.” *Environmental Science & Technology* 48 (13): 7612–24. doi:10.1021/es5010347.

Franklin Associates. 2011. *Cradle-to-Gate Life Cycle Inventory of Nine Plastic Resins and Four Polyurethane Precursors*. The Plastics Division of the American Chemistry Council Prairie Village, KS, USA.

Glauser, James. 2011. “CEH Marketing Research Report : Ammonium Sulfate.” SRI Consulting.

GREET. 2014. *GREET Model : Argonne National Laboratory Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation*. Argonne National Laboratory.

Haglund, Davis. 1999. *Life Cycle Inventory(LCI) of Fertiliser Production: Fertiliser Products Used in Sweden and Wester Europe*.

IPNI. 2012. “Nutrient Source Specifics : Kieserite.” #23#12025. International Plant Nutrition Institute. https://www.ipni.net/publication/nss.nsf/0/7CDEEAE379859BEF852579AF0076992C/$FILE/NSS-23%20Kieserite.pdf.

Jungbluth, Niels. 2008. “Life Cycle Inventory of Sodium Acetate and Expanded Graphite Short Report.” Germany: HEIG-VD / LESBAT.

Kim, Seungdo. 2015. “Enzymes for Pharmaceutrical Applications - a Cradle-to-Gate Life Cycle Assessment.”

Kim, Seungdo, Concepción Jiménez-González, and Bruce E. Dale. 2009. “Enzymes for Pharmaceutical Applications—a Cradle-to-Gate Life Cycle Assessment.” *The International Journal of Life Cycle Assessment* 14 (5): 392–400. doi:10.1007/s11367-009-0081-9.

Malveda, Michael, and Chiyo Funada. 2010. “CEH Marketing Research Report : Acetic Acid.” SRI Consulting.

Merza, Khalida S., Hadi D. Al-Attabi, Zaid M. Abbas, and Hashim A. Yusr. 2012. “Comparative Study on Methods for Preparation of Gold Nanoparticles.” *Green and Sustainable Chemistry* 2 (01): 26.

Papagianni, Maria, Frank Wayman, and Michael Mattey. 2005. “Fate and Role of Ammonium Ions during Fermentation of Citric Acid by Aspergillus Niger.” *Applied and Environmental Microbiology* 71 (11): 7178–86. doi:10.1128/AEM.71.11.7178-7186.2005.

Pisarczyk, Kenneth. 2000. “Manganese Compounds.” In *Kirk-Othmer Encyclopedia of Chemical Technology*. John Wiley & Sons, Inc. http://onlinelibrary.wiley.com/doi/10.1002/0471238961.1301140716091901.a01.pub2/abstract.

Seeger, Margarete, Walter Otto, Wilhelm Flick, Friedrich Bickelhaupt, and Otto S. Akkerman. 2000. “Magnesium Compounds.” In *Ullmann’s Encyclopedia of Industrial Chemistry*. Wiley-VCH Verlag GmbH & Co. KGaA. http://onlinelibrary.wiley.com/doi/10.1002/14356007.a15_595.pub2/abstract.

Shuler, Michael L., and Fikret Kargi. 2002. *Bioprocess Engineering*. Prentice Hall New York. http://libvolume2.xyz/biotechnology/semester4/bioprocessprinciplesandcalculations/unitsanddimensions/unitsanddimensionsnotes1.pdf.

Sigma Aldrich. 2015a. “‘Microbiology Products.’ Sigma-Aldrich.” *“Microbiology Products.” Sigma-Aldrich*. a. http://www.sigmaaldrich.com/analytical-chromatography/microbiology/microbiology-products.html?TablePage=8657623.

Sigma Aldrich. 2015b. “Sodium Acetate Anhydrous, for Molecular Biology.” *“Microbiology Products.” Sigma-Aldrich*. b. http://www.sigmaaldrich.com/catalog/product/sial/s2889?lang=en&region=US.

Suresh, Bala, and Chiyo Funada. 2012. “CEH Marketing Research Report : Sodium Sulfate.” IHS Inc.

Tanguler, Hasan, and Huseyin Erten. 2008. “Utilisation of Spent Brewer’s Yeast for Yeast Extract Production by Autolysis: The Effect of Temperature.” *Food and Bioproducts Processing* 86 (4): 317–21. doi:10.1016/j.fbp.2007.10.015.

von Plessen, Helmold. 2000. “Sodium Sulfates.” In *Ullmann’s Encyclopedia of Industrial Chemistry*. Wiley-VCH Verlag GmbH & Co. KGaA. http://onlinelibrary.wiley.com/doi/10.1002/14356007.a24_355/abstract.

Wagner, Frank S., and Updated by Staff. 2000. “Acetic Acid.” In *Kirk-Othmer Encyclopedia of Chemical Technology*. John Wiley & Sons, Inc. http://onlinelibrary.wiley.com/doi/10.1002/0471238961.0103052023010714.a01.pub3/abstract.

Wayne Richardson, H. 2000. “Copper Compounds.” In *Kirk-Othmer Encyclopedia of Chemical Technology*. John Wiley & Sons, Inc. http://onlinelibrary.wiley.com/doi/10.1002/0471238961.0315161618090308.a01.pub2/abstract.

Weston, Charles W., John R. Papcun, and Maurice Dery. 2000. “Ammonium Compounds.” In *Kirk-Othmer Encyclopedia of Chemical Technology*. John Wiley & Sons, Inc. http://onlinelibrary.wiley.com/doi/10.1002/0471238961.0113131523051920.a01.pub2/abstract.

Zapp, Karl-Heinz, Karl-Heinz Wostbrock, Manfred Schäfer, Kimihiko Sato, Herbert Seiter, Werner Zwick, Ruthild Creutziger, and Herbert Leiter. 2000. “Ammonium Compounds.” In *Ullmann’s Encyclopedia of Industrial Chemistry*. Wiley-VCH Verlag GmbH & Co. KGaA. http://onlinelibrary.wiley.com/doi/10.1002/14356007.a02_243/abstract.