ANL/ESD-14/12

# Development of GREET Catalyst Module

Energy Systems Division

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September 2014

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# Development of GREET Catalyst Module

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## 1. BACKGROUND

Catalysts are critical inputs for many pathways that convert biomass into biofuels. Energy consumption and greenhouse gas (GHG) emissions during the production of catalysts and chemical inputs influence the life-cycle energy consumption, and GHG emissions of biofuels and need to be considered in biofuel life-cycle analysis (LCA).

In this report, we develop energy and material flows for the production of three different catalysts (tar reforming, alcohol synthesis, Zeolite Socony Mobil-5 [ZSM-5]) and two chemicals (olivine, dimethyl ether of polyethylene glycol [DEPG]). These compounds and catalysts are now included in the Greenhouse Gases, Regulated Emissions and Energy Use in Transportation (GREET™) catalyst module. They were selected because they are consumed in existing U.S. Department of Energy (DOE) analyses of biofuel processes. For example, a thermochemical ethanol production pathway (indirect gasification and mixed alcohol synthesis) developed by the National Renewable Energy Laboratory (NREL) uses olivine, DEPG, and tar reforming and alcohol synthesis catalysts (Dutta et al., 2011). ZSM-5 can be used in biofuel production pathways such as catalytic upgrading of sugars into hydrocarbons (Biddy and Jones, 2013). Other uses for these compounds and catalysts are certainly possible.

In this report, we document the data sources and methodology we used to develop material and energy flows for the catalysts and compounds in the GREET catalyst module. In Section 2 we focus on compounds used in the model Dutta et al. (2011) developed. In Section 3, we report material and energy flows associated with ZSM-5 production. Finally, in Section 4, we report results.

# 2. CHEMICALS FOR INDIRECT GASIFICATION AND MIXED ALCOHOL SYNTHESIS

Dutta et al. (2011) developed a process model for indirect gasification of pine to produce ethanol and mixed alcohols. In this process, olivine serves as the heat transfer medium for the indirect gasification of the biomass. During gasification, syngas (CO and $H_2$) forms along with char and tar, which adhere to the olivine. The olivine is recovered and the char and tar are burned off with oxygen to reheat the olivine substrate. DEPG is used to remove most of the $H_2S$ and a portion of the $CO_2$ generated during gasification. Tars, methane, and light hydrocarbons are reformed to syngas in a circulating, fluidized, solid catalyst system that resembles a small-scale fluid catalytic cracker (FCC), complete with reforming and regeneration operations in separate beds. Finally, the syngas is converted to yield ethanol and mixed alcohols through a catalytic alcohol synthesis step using an alcohol synthesis catalyst.

## 2.1 Olivine

Olivine is a mineral form of magnesium-iron silicates. It has a high melting point and stores heat well. Accordingly, it is commonly used in high-temperature applications, such as indirect gasification. Olivine is commercially available in the United States, but only roughly one-third is produced domestically; the balance is imported from Norway, which has a large reserve of olivine ore (Kramer, 2001). We use these shares in GREET when developing the energy and material flows of olivine production.

Olivine needs very little processing before it can be used in a chemical process, so the main steps in its production are mining, size reduction, and transportation. We include the latter step because of the significant transportation distance between Norway and the United States. Table 1 contains mining energies for several different metals from the GREET vehicle cycle module (GREET 2). The mining energies for these different metals are comparable, so we adopt their average for the mining of olivine (2.8 mmBtu/ton). It was also necessary to estimate the breakdown of the total mining energy among different energy types such as diesel and natural gas. We did so on the basis of the energy type shares for metals mining in GREET. The share of diesel fuel ranges from 19% to 48% in Table 1. To be conservative, we used the lower end of this range because production of 1 mmBtu electricity is generally more energy intensive than production of 1 mmBtu of diesel fuel. We assumed that the diesel fuel consumption includes that for beneficiation, which is generally the case for metals in GREET 2. This assumption should not greatly affect the estimate of olivine mining energy because olivine requires minimal processing.

**Table 1 Energy consumption for metal mining (GREET2)**

| Metal | Energy Input (mmBtu/ton) | Non-electric Share |
|---|---|---|
| Copper | 2.15 | 48% Diesel |
| Iron ore | 1.80 | 10.8% NG, 10.2% Oil |
| Lead | 2.59 | 19% Diesel |
| Manganese | 3.72 | 19% Diesel |
| Nickel | 2.66 | 42.7% Oil, 37.5% Natural Gas |
| Zinc | 3.72 | 19% Diesel |

The remaining step in the olivine supply chain is to transport it to the biorefinery. For 1 ton of olivine, we assume that the portion produced in the United States travels by rail for 100 miles. We selected this distance because 100 miles separates an olivine mine and processing facility in the State of Washington. The Norwegian olivine travels across the ocean by ocean tanker for 3,700 miles (the distance between Oslo and New York City) and then domestically by rail for 100 miles (the distance from New York City to Bethlehem, Pennsylvania, where more than half of the imported olivine is consumed for steel production [Kramer, 2001]). The energy intensities of rail and ocean tanker transportation in GREET are 270 Btu/ton-mile and 43 Btu/ton-mile, respectively. Tankers consume residual oil, while locomotives burn diesel. Table 2 reports the purchased energy consumed during olivine production. Purchased energy is the actual amount of energy consumed at the olivine production facility. From these inputs, GREET calculates the full fuel cycle energy consumed in olivine production on the basis of GREET data for upstream impacts of producing diesel, residual oil, and natural gas (NG).

**Table 2 Purchased energy inputs to olivine production**

| Fuel Type | Mining (mmBtu/ton) | Transportation (mmBtu/ton) |
|---|---|---|
| Diesel | 0.5 | 0.03 |
| Residual oil | 0 | 0.11 |
| Electricity | 2.3 | 0 |
| Total (Direct) | 2.8 | 0.14 |

## 2.2 DEPG

DEPG is a specific form of polyethylene glycol with functional end groups that aid in capturing $H_2S$ and $CO_2$. To produce DEPG, ethylene oxide is polymerized into polyethylene glycol. The energy and material flow for production of ethylene oxide is from the GREET bioproducts module (Dunn et al., 2014a). The purchased energy consumed in the polymerization of polyethylene terephthalate, documented in an American Chemistry Council-sponsored life cycle assessment of polymers (Franklin Associates, 2011), is used as a representation of the energy consumed in ethylene oxide polymerization. Overall, the purchased energy consumed in

the production of 1 ton of DEPG is 0.0015 mmBtu diesel fuel, 2.4 mmBtu NG, 0.96 mmBtu coal, and 0.33 mmBtu electricity (Franklin Associates, 2011).

## 2.3 Tar Reforming Catalyst

The basis of the structure of the tar reforming catalyst is the structure from the Magrini-Bair et al. (2007) report. The catalyst is assumed to be composed of 5% nickel oxide (NiO), 4% potassium oxide ($K_2O$), and 8% magnesium oxide (MgO) on an 84% alumina ($Al_2O_3$) support (all percentages given by weight). An active alumina support is first prepared by drying and calcining an alumina solution at 600°C. After cooling to about 80°C, the support is wetted with an aqueous solution consisting of nickel nitrate [$Ni(NO_3)_2$], magnesium nitrate [$Mg(NO_3)_2$] and potassium nitrate ($KNO_3$). Finally, the mixture is calcined to yield the tar reforming catalyst that contains the oxidized form of the metals (Lloyd, 2011).

Among the material inputs to the tar reforming catalyst, the material and energy flow data for $KNO_3$ and $Al_2O_3$ exist in GREET. $Ni(NO_3)_2$ and $Mg(NO_3)_2$ are assumed to be produced by reacting nickel and magnesium metal with nitric acid, respectively. The energy and material flow data for the production of nickel, magnesium, and nitric acid are available in GREET. Finally, the energy consumption of the final calcining process is 2 mmBtu/ton catalyst based on Dunn et al. (2014b). This energy is assumed to be provided by a NG kiln with an efficiency of 80%.

## 2.4 Alcohol Synthesis Catalyst

The composition of the alcohol synthesis catalyst is approximated from U.S. Patent 4,882,360 (Stevens, 1989). It is assumed to be composed (all percentages given by weight) of 12% molybdenum oxide ($MoO_2$), 2% potassium oxide ($K_2O$), 11% cobalt oxide (CoO), and 68% carbon support (activated carbon). The remaining weight is assumed to be sulfur from hydrogen sulfide, which displaces oxygen during chemical reduction of the surface. The catalyst is prepared by contacting activated carbon with a hot aqueous solution of soluble Mo salt (i.e., ammonium heptamolybdate) and cobalt nitrate [$Co(NO_3)_2$] in a phosphoric acidic solution. After drying, the solids are contacted with the caustic KOH solution and subsequently dried. The resulting catalyst is then sulfided (Stevens, 1989).

To build the material and energy flows in the alcohol synthesis catalyst supply chain, we relied on existing GREET data in several cases, such as for KOH. $Co(NO_3)_2$ is produced by reacting CoO with nitric acid (Richardson, 2000), and the energy and material flow data for production of both CoO and nitric acid are available in GREET. Ammonium heptamolybdate is obtained by reacting ammonia solution with $MoO_3$, while $MoO_3$ is produced by calcining $MoS_2$ ore (Stiefel, 2000). GREET does not include data specific to molybdenum compounds. $MoS_2$ ore, however, frequently coexists and is co-mined with copper. Therefore, the mining data for copper (which are available in GREET) are used as a proxy for $MoS_2$ production. Energy consumption for calcining $MoS_2$ and for the final calcining step are each 2 mmBtu/ton reactant, provided by an 80% efficient natural gas kiln (Dunn et al., 2014b). In the United States, sulfur is mainly produced as a low-value by-product of petroleum refineries and from purification of NG. We

assign refinery energy consumption and emissions to the main, high-value refinery and natural gas processing products and treat the by-product sulfur as burden-free (Johnson et al., 2013).

The catalyst module contains new data for the production of activated carbon. Although almost any carbonaceous material can be converted into an activated carbon product, the starting materials used in the vast majority of industrial production operations are coal, coke, wood chips or sawdust, coconut shells, petroleum fractions and peat (Camara et al., 1999). For catalysis applications of activated carbon, very low levels of impurities are required which limits the possible starting materials to those capable of yielding a high-purity carbon product. Petroleum fractions and peat contain impurities that make them unsuitable as a feedstock for activated carbon. We therefore assume activated carbon is derived from a woody biomass source and adopt existing GREET data for the collection and processing of forest residue (Wang et al., 2013). The first step in the production of activated carbon from wood chips is the slow pyrolysis of the chips to yield biochar. The yield of biochar from pyrolysis is assumed to be 30% (Wang et al., 2014). The pyrolysis process produces flue gas and bio-oil that could be combusted to generate energy. The slow pyrolysis of the wood chips could therefore be energy self-sufficient, possibly producing excess energy depending on the heat integration (Wang et al., 2014). This extra energy could be applied towards the second step in the production of activated carbon (the activation step) or for other uses. Without precise information on heat integration or energy use at an actual facility producing activated carbon, however, we adopt the conservative assumption that the extra energy is discarded. Biochar can be activated with physical or chemical techniques. The most common method is a simple thermal treatment (physical activation) with an oxidizing gas, most often steam, $CO_2$ or a combination of both (Camara et al., 1999). Based on a patent US 20090317320 A1 (Srinivasachar et al., 2009), we assume the biochar is activated with steam at a temperature of 875 °C with a residence time of 90 minutes and a conversion yield of 67% from biochar to activated carbon. The mass ratio of biochar/ steam is 0.92:1, and the heat needed for the production of steam and the activation process is calculated to be 10 mmBtu/ ton activated carbon (Srinivasachar et al. 2009). We assume this heat is provided by a natural gas-fired kiln with an efficiency of 80%.

# 3. ZSM-5 CATALYST

ZSM-5 is an aluminosilicate zeolite. It is widely used in the petroleum industry as a heterogeneous catalyst, and it can also be used for catalyzing chemical reactions for biofuel production.

According to information in patent literature and limited publications (Stamires et al., 2007; Stockwell et al., 2005; Harris et al., 2004; Van Der Zon and Hilgers, 2008; Venuto and Habib, 1979), ZSM-5 composition can vary widely, and it is often combined with fillers and binders (e.g., silica gel and kaolin) when used as a catalyst. To differentiate neat ZSM-5 and the mixture of ZSM-5 with fillers and binders, we refer to the latter as ZSM-5 catalyst and the former as ZSM-5.

We used publicly available information to estimate ZSM-5 catalyst consumption rates in a generic biorefinery. A 60,000-barrel/day FCC unit processing a typical mixture of vacuum gas oils contains 450–500 tons of ZSM-5 catalyst (Kent, 2013). This loading converts to about 25–30 tons of catalyst in a biorefinery FCC as proposed by Biddy and Jones (2013) that consumes 2,205 dry tons/day (2,000 metric tonne/day) of biomass and produces about 3,500 barrels/day of biofuel. Assuming a 2% replacement rate for the catalyst (Kent, 2013; Pryor, 2014), the daily consumption of the catalyst is estimated to be 0.6 tons, or 1,200 lb. Recovery of spent ZSM-5 is generally considered economically infeasible and is not widely practiced (Bertolancini, 2014). Although details regarding the function of the zeolite, fillers, and binders are available (Venuto and Habib, 1979; Sadeghbeigi, 2000), the detailed formulation of ZSM-5 catalyst is difficult to obtain from specific catalyst manufacturers. Typically, a ZSM-5 catalyst contains at most 50 wt% ZSM-5 (Stockwell et al., 2005; Harris et al., 2004; Stamires et al., 2007). On the basis of this information, we assume the ZSM-5 catalyst consists of 50% ZSM-5, 25% silica gel, and 25% binder (kaolin).

## 3.1 Preparation of ZSM-5

Figure 1 outlines the steps in the preparation of ZSM-5 catalyst (Lloyd 2011). Material flows in the production of ZSM-5 are listed in Table 3. The input materials listed in Table 3 are autoclaved for 5 days, then filtered and washed six times with hot deionized water. After that, the filter cake is blended with $SiO_2$ gel and kaolin with sufficient water for spray drying. The final step is solids calcination (Argauer and Landolt, 1972; Mei et al., 2008; New Logic Research Inc., 2014).

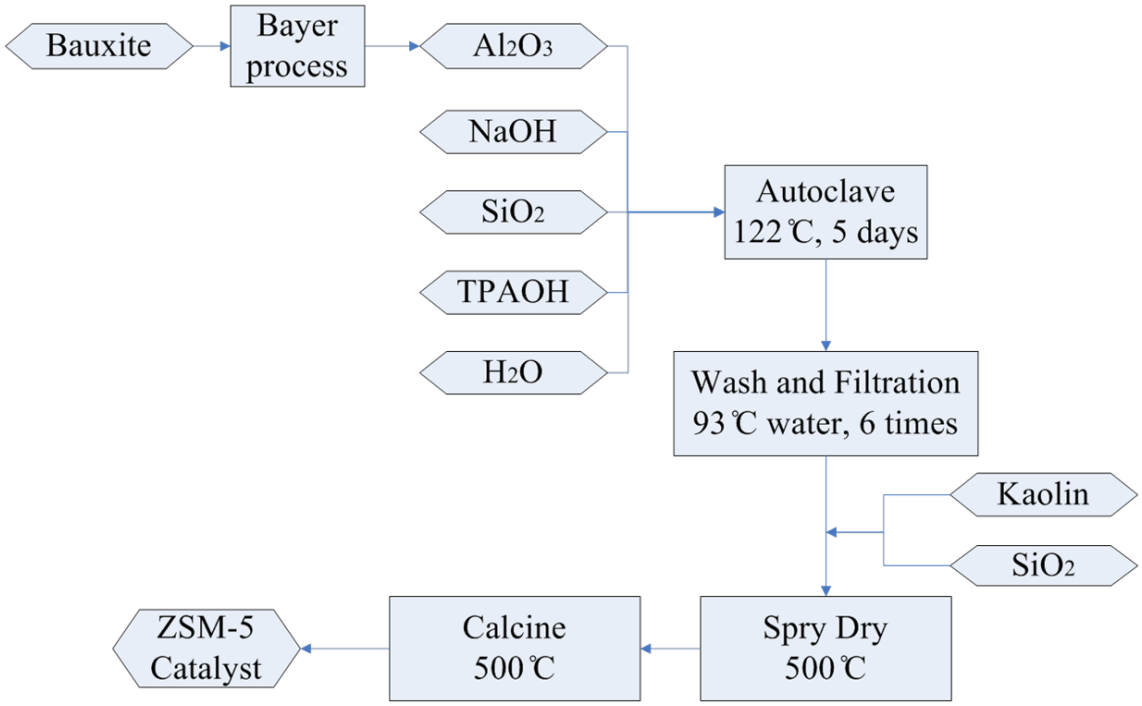


**Figure 1 Diagram for preparation of ZSM-5 catalyst**

**Note: TPAOH= N-tetrapropylammonium hydroxide [$(CH_3CH_2CH_2)_4N^+OH^-$]**

**Table 3 Inputs and outputs for the production of 600 lb/day ZSM-5 (Argauer and Landolt, 1972)**

| Chemical | Amount (lb/day) |
|---|---|
| *Inputs* | |
| TPAOH | 588 |
| NaOH | 31 |
| $Al_2O_3$ | 33 |
| $SiO_2$ | 562 |
| $H_2O$ | 2,787 |
| **Total** | **4,000** |
| *Outputs* | |
| ZSM-5 ($Na_2O \cdot 2\ Al_2O_3 \cdot 65\ SiO_2$) | 600 |

Few data were available to support the calculation of the energy intensity of ZSM-5 production. To generate an estimate of this energy intensity, we used engineering calculations and calculated the energy consumed in each of the process steps. Table 4 shows the estimated energy consumption for each step and lists the assumptions used in the engineering calculations in which process heat is assumed to be provided by steam produced from an 80% efficient natural gas boiler.

**Table 4 Energy consumption during ZSM-5 preparation**

| Step | Purchased Energy Consumption (Btu) Natural Gas | Electricity | Bases for Engineering Calculations |
|---|---|---|---|
| Autoclave | 1,900,000 | – | 4,000 lb of gel mixture is heated to 122°C for 5 days. We assumed heat loss is 20% per day. |
| Wash and filtration | 4,200,000 | 110,000 | 4,000 lb of water is heated to 93°C and used to wash solids six times. 3.93 kW are consumed for 8 hours/day. |
| Binder/filler | 5,200,000 | – | Binder and filler are heated and washed using the same parameters for ZSM-5. |
| Spray drying | 5,400,000 | – | A gel mixture (with 65% moisture content) is dried with 500°C vent gas. The calculation assumes 10% heat loss |
| Calcining | 1,300,000 | – | 1,800 lb gel is heated from 122°C to 500°C at 0.6 Btu/lb °F. The heat loss is 40%. |
| **Total** | **18,000,000** | **110,000** | For producing 600 lb ZSM-5 |
| **Total (mmBtu/ton ZSM-5)** | **60** | **0.36** | GREET inputs |

Among the chemical inputs in Table 3, energy and material flows of $Al_2O_3$ and NaOH are available in GREET. We developed new data to characterize the production of $SiO_2$ gel. The first step in this process is sand extraction, with an energy consumption of 0.16 mmBtu electricity/ton $SiO_2$ (Boustead and Hancock, 1979). The sand is calcined with $Na_2CO_3$ to yield $Na_2O{\cdot}SiO_2$ (Reaction 1), and then $H_2SO_4$ is added to form an aqueous salty solution containing silica colloids (Reaction 2). The $Na_2SO_4$ is rinsed away with water, and the $SiO_2$ gel is spray dried. The energy consumption for calcining, washing, and spray drying was estimated on the basis of process information from New Logic Research, Inc. (2014), to be 15.2 mmBtu NG/ ton $SiO_2$. Engineering calculation methods used to derive this estimate are the same as those in Table 4:

$$SiO_2+Na_2CO_3 \rightarrow Na_2O{\cdot}SiO_2+CO_2 \quad (1)$$
$$Na_2O{\cdot}SiO_2+H_2SO_4 \rightarrow SiO_2+H_2O+Na_2SO_4 \quad (2)$$

There is little information regarding the supply chain for TAPOH that can be used to construct the material and energy intensity of this compound. We estimated these parameters on the basis of the limited information in the literature and engineering calculations. The following reactions lead to the formation of TPAOH (Weston et al., 2003; Papa, 2000).

$$H_2C = CH_2 + CO + H_2 \rightarrow CH_3CH_2CHO \qquad \Delta H = -128.3 \text{ kJ/mol} \quad (3)$$
$$CH_3CH_2CHO + H_2 \rightarrow CH_3CH_2CH_2OH \qquad \Delta H = -68.9 \text{ kJ/mol} \quad (4)$$
$$3CH_3CH_2CH_2OH + PCl_3 \rightarrow 3CH_3CH_2CH_2Cl+H_3PO_3 \qquad \Delta H = -207.4 \text{ kJ/mol} \quad (5)$$

$$3CH_3CH_2CH_2OH + NH_3 \rightarrow (CH_3CH_2CH_2)_3N + 3H_2O \qquad \Delta H = -74.9 \text{ kJ/mol} \qquad (6)$$
$$(CH_3CH_2CH_2)_3N + CH_3CH_2CH_2Cl \rightarrow (CH_3CH_2CH_2)_4N^+Cl^- \qquad (7)$$
$$(CH_3CH_2CH_2)_4N^+Cl^- + NaOH \rightarrow (CH_3CH_2CH_2)_4N^+OH^- + NaCl \qquad (8)$$

The overall TPAOH synthesis reaction is

$$4H_2C = CH_2 + 4CO + 8H_2 + \frac{1}{3}PCl_3 + NH_3 + NaOH \rightarrow$$
$$(CH_3CH_2CH_2)_4N^+OH^- + 3H_2O + \frac{1}{3}H_3PO_3 + NaCl \qquad (9)$$

It is difficult to estimate the energy consumption for Reactions 3–8. Calculating the heats of reaction for Reactions 3–6, however, reveals they are all exothermic (Perry and Green, 1997). We therefore assume no energy input is required for these reactions to proceed. We estimated the energy input for Reaction 7 on the basis of the work of Weston et al. (2003). It is assumed that to carry out Reaction 7, the reactants are heated to 100°C for 32 hours with 40% heat loss. The resulting energy consumption is 0.43 mmBtu/ton, which we assume to be provided by steam from an 80% efficient NG boiler. Reaction 8 is a reaction in solution and we assume it consumes no energy.

Among the reactants in the aggregated Reaction 9, energy and material flow for ethylene, $NH_3$, and NaOH are all available in GREET. According to George (2000), CO is usually produced in syngas production, along with $H_2$ and other gases. We assume NG-derived syngas provides the CO and $H_2$ required in Reaction 9 (Dunn et al., 2014a).

We developed the material and energy intensity of $PCl_3$ on the basis of information in Greenwood and Earnshaw (1997) and Threlfall (1951). This compound is prepared industrially by the reaction of chlorine with a refluxing solution of white phosphorus in phosphorus trichloride. $PCl_3$ is removed continuously from the reflux solution to avoid the formation of $PCl_5$ (Greenwood and Earnshaw, 1997). White phosphorus ($P_4$) is produced by calcining phosphorous rock with sand and charcoal, as shown in Reaction 10 (Threlfall, 1951):

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow 6CaSi_3O_3 + 10CO + P_4 \qquad (10)$$
$$P_4 + 6Cl_2 \rightarrow 4PCl_3 \qquad (11)$$

Among the reactants in Reactions 10 and 11, energy and material flows of $Ca_3(PO4)_2$, C (coke) and $Cl_2$ exist in GREET. We have developed energy and material flows for $SiO_2$ in this analysis. The calcining energy to produce $P_4$ (Reaction 10) is assumed to be 2 mmBtu/ton reactant provided by an 80% efficient natural gas boiler (Dunn et al. 2014b). Reaction 11 is an exothermic reaction and we assume it consumes no energy.

The aggregated material inputs for TPAOH production are shown in Table 5.

**Table 5 Material inputs for TPAOH production**

| Inputs | (ton/ton TPAOH) |
|---|---|
| $C_2H_4$ | 0.55 |
| Syngas* | 1.15 |
| $NH_3$ | 0.08 |
| $PCl_3$ | 0.68 |
| NaOH | 0.59 |

*Contains 0.55 ton CO and 0.09 ton $H_2$ per 1.15 ton syngas.

## 3.2 Preparation of Fillers and Binders

The catalyst filler is $SiO_2$ gel, for which we report material and energy intensity in Section 3.1. We model the energy and material flows in the production of the kaolin binder (Figure 2) on the basis of U.S. patent 7,922,806 B2 (Yan et al., 2011).

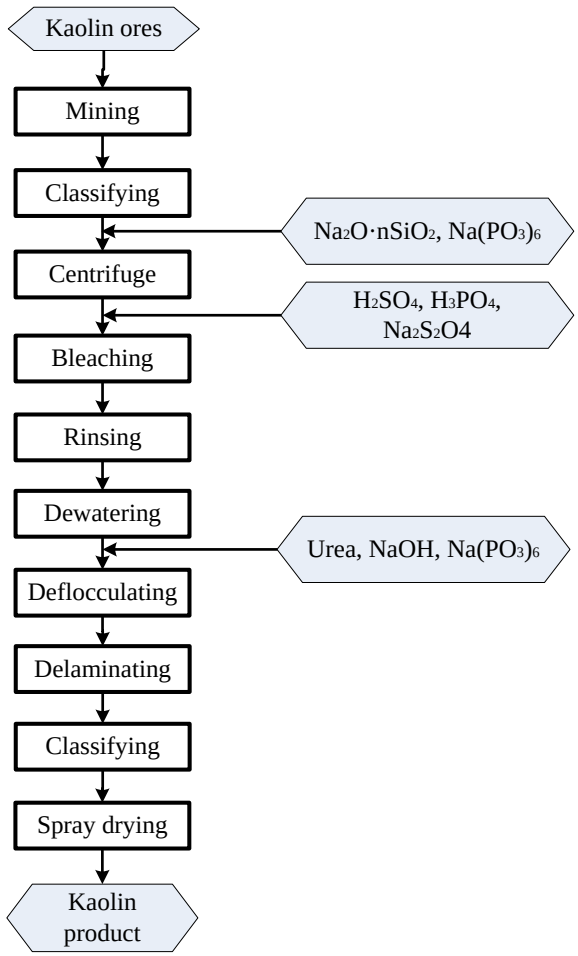


**Figure 2 Diagram for production of kaolin**

Energy and materials consumption for the production of kaolin are shown in Tables 6 and 7, respectively. For the mining step, we assume that kaolin ore is as energy intensive to mine as olivine. Recall the energy intensity of olivine mining was estimated to be 2.3 mmBtu diesel and 0.5 mmBtu electricity per ton (Section 2.1). This energy intensity includes classifying to remove sand.

In the classifying step, sand is removed from kaolin with a horizontal spiral sedimentation centrifuge. We assume this stage is 90% efficient. We adopt the same efficiency for the subsequent centrifuge step. That is, we assume that 10% of the mass of kaolin entering these steps is not recovered. We turned to existing centrifuge and dewatering (with pressure filtration) energy consumption data in GREET's Algae Process Description (APD) to estimate the energy consumption of these steps as 8 kWh/$m^3$ influent and 7.26 kWh/$m^3$ influent, respectively (Frank et al., 2011). Stirring drives the energy use during bleaching, deflocculating, and delaminating. The energy consumption for homogenization (36.7 kWh/$m^3$ processed volume) is again adopted from the APD (Frank et al., 2011) to account for the stirring energy consumption. Energy consumption for rinsing is approximated with that for leaching (Dunn et al., 2014b). Energy consumption of spray drying is estimated by applying the same method we used

for this step of ZSM-5 production (Table 5). Taking into account kaolin losses at every stage, 1 dry ton of kaolin ore is consumed in the production of 0.87 dry ton of final kaolin product.

**Table 6 Energy consumption during kaolin production**

| | Energy Consumption (mmBtu/ton kaolin) | | |
|---|---|---|---|
| Step | NG | Electricity | Diesel |
| Mining and classifying | – | 2.6 | 0.61 |
| Centrifuge | – | 0.20 | – |
| Bleaching | – | 0.35 | – |
| Rinsing | – | 0.14 | – |
| Dewatering | – | 0.07 | – |
| Deflocculating | – | 0.20 | – |
| Delaminating | – | 0.20 | – |
| Spray drying | 1.9 | – | – |
| Total | 1.9 | 3.8 | 0.61 |

**Table 7 Materials inputs for kaolin production**

| Inputs | ton/ton kaolin |
|---|---|
| $(NaPO_3)_6$ | 0.038 |
| $H_2SO_4$ | 0.0062 |
| $Na_2S_2O_4$ | 0.019 |
| $H_3PO_4$ | 0.0062 |
| NaOH | 0.038 |
| Urea | 0.019 |
| $SiO_2$ | 0.0076 |

Of the material inputs in Table 7, GREET contains data for $H_2SO4$, $H_3PO4$, urea and NaOH. This report develops material and energy flows for $SiO_2$ (Section 3.1).

$(NaPO_3)_6$ is not currently in GREET. We estimate its associated material and energy flows as follows, beginning with its synthesis in Reaction 12 through melting $NaH_2PO_4$ (EPA, 2000):

$$6NaH_2PO_4 \rightarrow (NaPO_3)_6 + 6H_2O \quad (12)$$

Because $NaH_2PO_4$ is chemically similar to $KH_2PO_4$, we adopt GREET data for the latter compound in this analysis. The energy for melting $NaH_2PO_4$ is assumed to be 2 mmBtu/ton reactant provided by an 80% efficient NG kiln (Dunn et al., 2014b).

We also needed to estimate new material and energy flow data for $Na_2S_2O_4$, which is produced through Reactions 13–15. First sulfur is oxidized to produce $SO_2$, and $NaHSO_3$ is generated by reacting $SO_2$ with NaOH. Next, zinc dust is reacted with $NaHSO_3$ to form $Na_2S_2O4$ (OECD SIDS, 2004):

$$S + O_2 \rightarrow SO_2 \quad (13)$$
$$SO_2 + NaOH \rightarrow NaHSO_3 \quad (14)$$
$$2NaHSO_3 + Zn \rightarrow Na_2S_2O4 + Zn(OH)_2 \quad (15)$$

The aggregated reaction is:

$$2S + 2O_2 + 2NaOH + Zn \rightarrow Na_2S_2O4 + Zn(OH)_2 \quad (16)$$

As discussed previously, sulfur is produced industrially as a co-product or waste for petroleum products and natural gas production and considered burden free (Johnson et al., 2013). The energy and material flow of NaOH and Zn is available in GREET. The calcining energy for Reaction 15 is assumed to be 2 mmBtu/ton reactants (Dunn et al., 2014b). This energy is assumed to be provided by NG with an efficiency of 80%.

# 4. SUMMARY

Table 8 summarizes the fossil fuel use and GHG emissions for the five compounds included in the GREET catalyst module. It is important to note that limited data necessitated reliance on engineering calculations and estimates to generate these results. In the case of ZSM-5 catalyst, the GHG emissions are dominated by the production of ZSM-5 (Figure 3). The contribution of ZSM-5 production to the cradle-to-gate GHG emissions is one order of magnitude higher than that from kaolin and $SiO_2$ gel as filler. Emissions associated with the energy consumed during ZSM-5 production contribute the most to overall ZSM-5 production emissions. Production of TPAOH and $SiO_2$ gel also contribute significantly.

To assess the sensitivity of results to changes in the cradle-to-gate GHG intensity of the inputs to ZSM-5 catalysts, we conducted a sensitivity analysis, varying these intensities individually by ±25%. It is important to note that the values that were varied in this analysis were the cradle-to-gate value for each input. For example, the value for kaolin incorporates the full fuel-cycle GHG emissions of the NG consumed in kaolin production and the GHGs emitted over the full supply chain of the urea consumed in producing kaolin. This variation in input GHG intensity resulted in at most a 9% change in the GHG intensity of the ZSM-5 catalyst. This catalyst's GHG intensity was most sensitive to the GHG intensity of TPAOH production. It was slightly less sensitive to the GHG intensity of the ZSM-5 production process and $SiO_2$ gel production, and relatively insensitive to the GHG intensity of kaolin production.

As the catalyst module is refined, we will continue to seek improved data for key drivers of ZSM-5 catalyst emissions, focusing on energy consumed in ZSM-5, TPAOH, and $SiO_2$ gel production. ZSM-5 is not currently integrated into any GREET biofuel pathways, but it is anticipated to be added to the catalytic sugars to hydrocarbons pathway once it is incorporated into GREET (Biddy and Jones, 2013). An important gap in our analysis of catalysts is the handling, treatment, and disposal of wastes generated in their production and use. We will investigate these aspects of the catalyst life cycle and refine the module to address them.

**Table 8 Fossil fuel use and GHG emissions of the compounds in the GREET catalyst module**

| Cradle-to-Gate Result | Alcohol Synthesis Catalyst | DEPG | Olivine | Tar Reforming Catalyst | ZSM-5 Catalyst |
|---|---|---|---|---|---|
| Fossil fuels (mmBtu/ton) | 30 | 60 | 5.5 | 40 | 100 |
| GHG (g $CO_2$e/ton) | 3,000,000 | 3,000,000 | 500,000 | 5,000,000 | 7,000,000 |

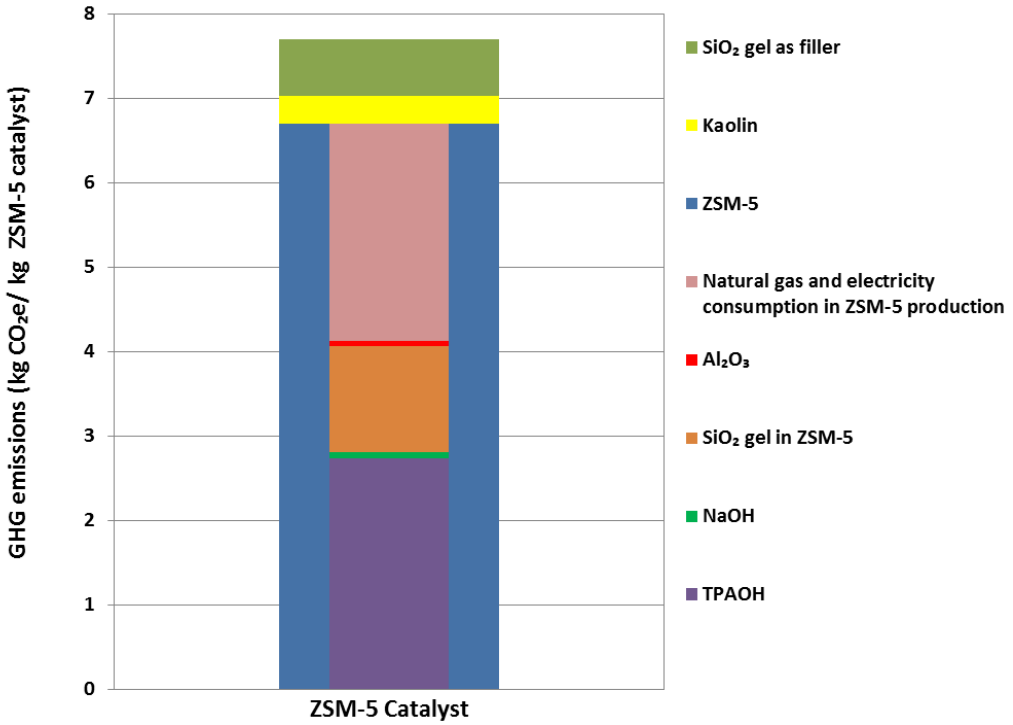


**Figure 3 Cradle-to-gate GHG emissions for ZSM-5 catalyst; emissions from ZSM-5 are broken up into five contributing factors**

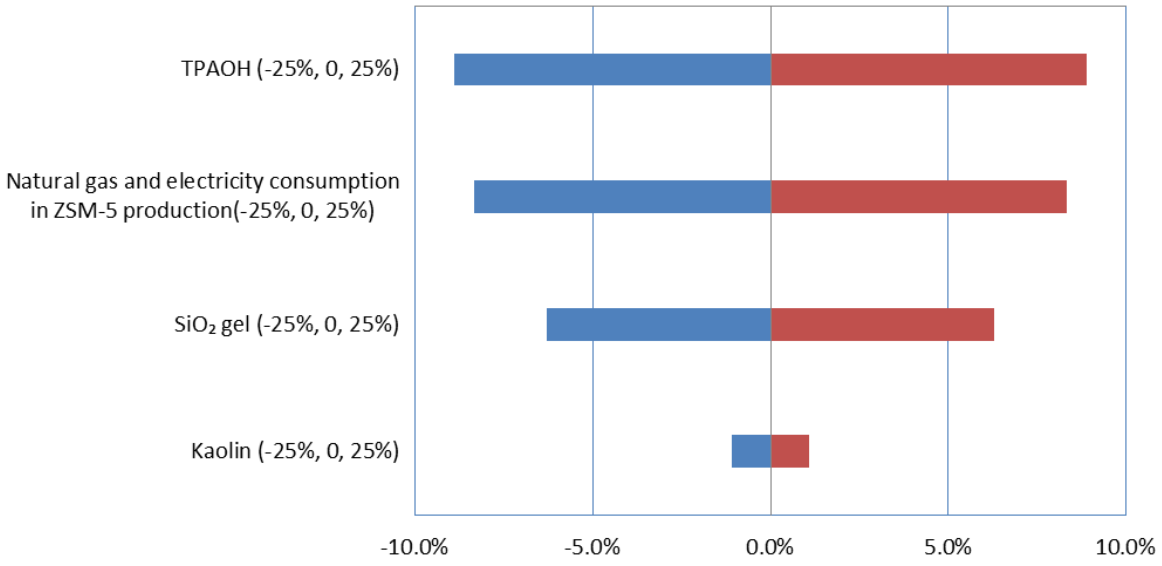


**Figure 4 Sensitivity analysis of ZSM-5 catalyst cradle-to-gate GHG emissions; baseline value is 7.7 kg $CO_2$e/kg ZSM-5 catalyst**

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