

Lightweight Materials for Automotive Application

An Assessment of Material Production Data for Magnesium and Carbon Fiber

Energy Systems Division

ABOUT ARGONNE NATIONAL LABORATORY

Argonne is a U.S. Department of Energy laboratory managed by UChicago Argonne, LLC under contract DE-AC02-06CH11357. The Laboratory's main facility is outside Chicago, at 9700 South Cass Avenue, Argonne, Illinois 60439. For information about Argonne and its pioneering science and technology programs, see www.anl.gov.

DOCUMENT AVAILABILITY

Online Access: U.S. Department of Energy (DOE) reports produced after 1991 and a growing number of pre-1991 documents are available free via DOE's SciTech Connect (<http://www.osti.gov/scitech/>)

Reports not in digital format may be purchased by the public from the National Technical Information Service (NTIS):

U.S. Department of Commerce National Technical Information
Service 5301 Shawnee Rd
Alexandra, VA 22312
www.ntis.gov
Phone: (800) 553-NTIS (6847) or (703) 605-6000
Fax: (703) 605-6900
Email: orders@ntis.gov

REPORTS NOT IN DIGITAL FORMAT ARE AVAILABLE TO DOE AND DOE CONTRACTORS FROM THE OFFICE OF SCIENTIFIC AND TECHNICAL INFORMATION (OSTI):

U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
www.osti.gov
Phone: (865) 576-8401
Fax: (865) 576-5728
Email: reports@osti.gov

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor UChicago Argonne, LLC, nor any of their employees or officers, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of document authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, Argonne National Laboratory, or UChicago Argonne, LLC.

Lightweight Materials for Automotive Application

An Assessment of Material Production Data for Magnesium and Carbon Fiber

by
M.C. Johnson and J.L. Sullivan
Energy Systems Division, Argonne National Laboratory

September 2014

CONTENTS

ACRONYMS.....	V
1 INTRODUCTION.....	1
2 MAGNESIUM METAL MARKET.....	3
2.1 Magnesium Metal Production.....	3
2.1.1 Thermal Route to Magnesium Metal.....	4
2.1.2 Electrolytic Production of Magnesium Metal.....	7
2.1.3 Summary of Primary Production of Magnesium.....	10
2.2 Cover Gas and Greenhouse Gases.....	11
2.3 Secondary Production of Magnesium.....	12
2.4 Casting and Molding.....	13
2.5 Summary.....	14
3 CARBON FIBER MARKET.....	15
3.1 Ammonia Production.....	16
3.2 Propylene Production.....	18
3.3 Acrylonitrile Production.....	19
3.4 Polyacrylonitrile Production.....	20
3.5 Carbon Fiber Production.....	21
3.6 Cumulative Energy Demand and GHG Emissions for CF Production.....	21
4 CONCLUSION.....	23
5 REFERENCES.....	25

FIGURES

1 Process steps included in our PCA for producing magnesium metal by the thermal and electrolytic approaches.....	4
2 Process steps included in PCAs for producing carbon fibers.....	16

TABLES

1 Inputs to Pidgeon (thermal) process for 1 kg magnesium ingot.....	5
2 Inputs to Bolzano (thermal) process for 1 kg magnesium ingot.....	6
3 Inputs to the Pidgeon process for 1 kg of magnesium ingot.....	7
4 Inputs to AMC electrolytic process for 1 kg magnesium ingot.....	8

TABLES (CONT.)

5	Energy and material inputs to the AMC electrolytic process per kilogram magnesium ingot	9
6	Purchased energy units and corresponding CED and GHG values for producing a kilogram of virgin magnesium ingot via the electrolytic and thermal approaches.	10
7	SF ₆ emission rates at various production stages per kilogram of magnesium	12
8	CED and GHG for molding/casting and finishing processes per kilogram of magnesium in part	14
9	Energy inputs for the production of a kilogram of ammonia in the U.S.	17
10	Purchased energy inputs for the production of a kilogram of propylene	19
11	Purchased energy inputs for the production of a kilogram of acrylonitrile.....	19
12	Materials, fuels, CED, and GHG for the production of a kilogram of carbon fiber from PAN fibers from our PCA data from Das.....	22

ACRONYMS

ACC	American Chemistry Council
AMC	Australian Magnesium Corporation
AN	Acrylonitrile
CED	cumulative energy demand
CF	carbon fiber
DOE	U.S. Department of Energy
GHG	greenhouse gas
REET	Greenhouse gases, Regulated Emissions, and Energy use in Transportation model
GWP	global warming potential
IEA	International Energy Agency
IMA	International Magnesium Association
LCA	life cycle assessment
LCI	life cycle inventory
LHV	lower heating value
MMA	methyl methacrylate
OPF	oxidized polyacrylonitrile fiber
PAN	polyacrylonitrile
PCA	process chain analysis
TFI	The Franklin Institute
UNIDO	United Nations Industrial Development Organization
USM	U.S. Magnesium

Lightweight Materials for Automotive Application

An Assessment of Material Production Data for Magnesium and Carbon Fiber

M.C. Johnson and J.L. Sullivan

1 INTRODUCTION

The use of lightweight materials in vehicle components, also known as “lightweighting,” can result in automobile weight reduction, which improves vehicle fuel economy and generally its environmental footprint. Materials often used for vehicle lightweighting include aluminum, magnesium, and polymers reinforced with either glass or carbon fiber. However, because alternative materials typically used for vehicle lightweighting require more energy to make on a per part basis than the material being replaced (often steel or iron), the fuel efficiency improvement induced by a weight reduction is partially offset by an increased energy for the vehicle material production. To adequately quantify this tradeoff, reliable and current values for life-cycle production energy are needed for both conventional and alternative materials.

Our focus here is on the production of two such alternative materials: magnesium and carbon fibers. Both these materials are low density solids with good structural properties. These properties have enabled their use in applications where weight is an issue, not only for automobiles but also for aerospace applications.

This report addresses the predominant production methods for these materials and includes a tabulation of available material and energy input data necessary to make them. The life cycle inventory (LCI) information presented herein represents a process chain analysis (PCA) approach to life cycle assessment (LCA) and is intended for evaluation as updated materials production data for magnesium and carbon fiber for inclusion into the Greenhouse gases, Regulated Emissions, and Energy use in Transportation model (GREET2_2012). The summary life-cycle metrics used to characterize the cradle-to-gate environmental performance of these materials are the cumulative energy demand (CED) and greenhouse gas emissions (GHG) per kilogram of material.

This page intentionally blank.

2 MAGNESIUM METAL MARKET

Magnesium (Mg) metal is used in aluminum-based alloys, magnesium-based structures like castings or wrought alloys, and iron and steel desulfurization (Kramer, 2012). When aluminum alloys containing magnesium are recycled, the metal remains with aluminum to remake aluminum alloys; it is not separated to pure magnesium. Old scrap is mostly sourced from used beverage containers (i.e., aluminum cans). In the U.S., approximately 155 thousand metric tons (kT) of magnesium metal was consumed in 2010. Aluminum alloys accounted for 23.8 kT of primary and 49.8 kT of secondary magnesium, assuming all aluminum-based alloy scrap that is recovered is remade into aluminum alloy (Kramer, 2010).

In 2010, the total magnesium-based supply (not aluminum alloys) in the U.S. was about 96 kT. Primary production in the U.S. accounted for 45 kT, and 22 kT of secondary production was from both domestic and imported scrap (Kramer, 2010). The remaining magnesium was imported as metal or alloys to make up the balance. Israel supplied most of the magnesium metal and alloy imports, 18 kT, with other countries supplying less than 1.5 kT each. These trade numbers vary over time, due especially to changes in tariffs and trade agreements. For example, Chinese imports of magnesium metal dropped from 5 kT in 2009 to 1.3 kT in 2010 (Kramer, 2010).

2.1 MAGNESIUM METAL PRODUCTION

Magnesium metal is produced by two main methods—electrolytic and thermal. The electrolysis process uses magnesium chloride (MgCl_2) as the base material, whereas the thermal process utilizes magnesium oxide (MgO). Chemical reactions can be used to convert a resource into the desired chemical raw material; for example, hydrochloric acid is reacted with magnesium oxide to make magnesium chloride for the electrolytic process. The process diagrams found in Figure 1 serve as the basis for our PCA of these two approaches for making magnesium.

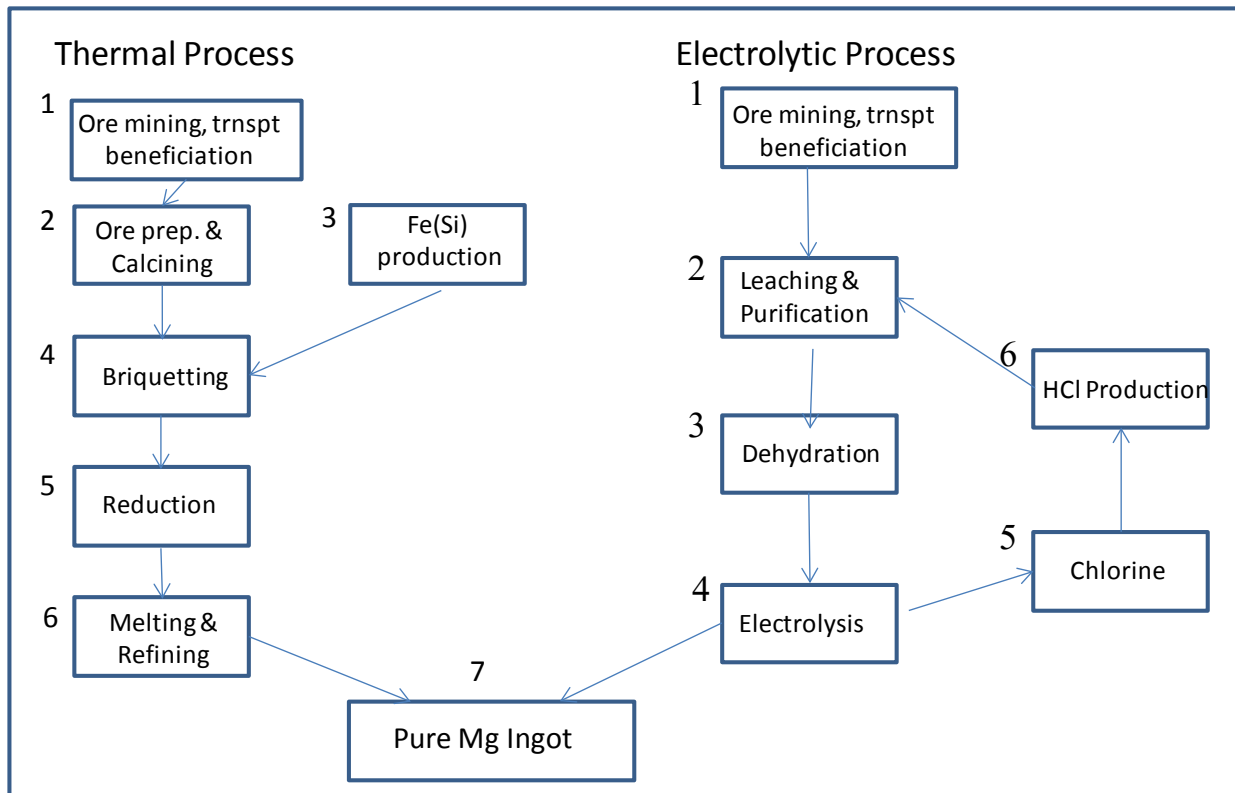
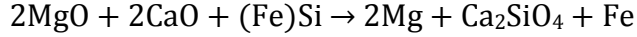


FIGURE 1 Process steps included in our PCA for producing magnesium metal by the thermal and electrolytic approaches

2.1.1 Thermal Route to Magnesium Metal

The majority of the world’s magnesium (85%) is produced in China by a thermal route known as the Pidgeon process (USGS, 2013), which is more economical than its electrolytic counterpart (Wulandari, et al., 2010). Magnesium output from China is around 800,000 kT per year. China has large coal resources as well as dolomite ($\text{CaMg}(\text{CO}_3)_2$), a magnesium ore. Other thermal routes are possible, like the Magnetherm and Bolzano processes, but they are minimally utilized. Currently, due to trade antidumping tariffs, Chinese-produced magnesium is not widely used in the U.S.

The Pidgeon process has been described by Ramakrishnan and Koltun (2004b). This process consists of feeding crushed magnesium ore (dolomite) to a calcining process (1000–1300°C) that produces dolime ($\text{CaO}\bullet\text{MgO}$). For each mole of magnesium, the calcination generates 2 moles of CO_2 (24 g Mg for 88 g CO_2). The calcined product is crushed and mixed with ferrosilicon and then formed into briquettes. Ferrosilicon is an alloy made by the reduction of silica sand with coke and iron scrap in an arc furnace at temperatures of 1600°C. The briquettes are fed to a batch vacuum reduction furnace run at 1160°C and 1–2 Pa, which releases magnesium vapor. Water-cooled condensate is used to collect the magnesium as pure solid (crown) before it is subsequently remelted and formed into ingots. The overall magnesium production equation is given below:



Life cycle analysis of the Pidgeon process was performed by Ramakrishnan and Koltun (2004b). The process steps and inputs for each step are included in Table 1. Wastes associated with the slag produced are not included. While reaction byproducts can be potentially used in plaster and brick production, such co-product benefits are undocumented at this time. Process energy fuels were estimated from given energy demands by using conversion factors and lower heating values (LHVs) for fuels given in GREET1. To facilitate a comparison between process designs, the briquetting and calcining processes are combined into a “feedstock preparation” step, and any transportation steps are rolled into the process step that it accompanies.

TABLE 1 Inputs to Pidgeon (thermal) process for 1 kg magnesium ingot (Ramakrishnan & Koltan, 2004b)

Step ID# ^a	Process Step	Output of Step	Diesel (liters)	Electricity (kWh)	Coal (kg)	Other Inputs
1	Mining ore and transportation	11.6 kg dolomite and 10.5 kg coal	0.106	0.067	–	–
2	Ore prep and Calcining	5.358 kg dolime	–	–	2	–
3	Ferrosilicon production	1.19 kg (Fe)Si _x	0.005	12.49	0.9	0.43 kg iron scrap 1.31 kg sand
4	Briquetting	6.678 kg pellets	–	0.181	–	1.703 kg CaF ₂ 0.426 kg mineral oil
5	Magnesium reduction	1.096 kg Mg crown	–	0.153	7.2	1.25 kg iron 0.72 kg brick 1.0 kg water
6,7	Ingot production	1 kg Mg ingot	–	–	0.3	0.05 kg sulfur
Totals			0.111	12.9	10.4	

^a See Figure 1.

A Chinese study analyzed the Pidgeon process from the perspective of changing the fuel sources in the future (Gao, et al., 2008). Their baseline scenario is representative of current Chinese production, which is compared here to Ramakrishnan and Koltun’s (2004b) results. Gao (2008) used a less concentrated form of dolomite ore, so 15 kg was used instead of 11.6 kg to get the requisite magnesium. Also, Gao (2008) used 11.9 kg coal, compared to 10 kg in Ramakrishnan and Koltun (2004b), and simultaneously reduced electricity from 12.9 to 1 kWh/kg-Mg. Furthermore, Gao reduced the CaF₂ requirement to 0.25 kg/kg-Mg, which is similar to the range that Ramakrishnan and Koltun (2004b) referenced (0.15–0.25 kg/kg-Mg), though they used 1.7 kg of CaF₂ in their data summary table.

Brazil produces 10–15 kT of Mg annually with the Bolzano process, a slight variant on the Pidgeon process. In this Bolzano process, the retort reactor for reduction is electrically heated to 1200°C at 400 Pa. The higher temperature allows for operating closer to atmospheric pressure (less vacuum necessary). The electricity grid in Brazil has an abundance of hydroelectric power, allowing for cheap electricity for processes and much reduced greenhouse gas and criteria air pollutant emissions over those associated with fossil fuel-derived electricity.

Cherubini et al. (2008) estimated the energy needs for the Bolzano process. Unfortunately, the Bolzano energy values listed in Table 2 represent only the summary given by Cherubini, which excludes the “ferrosilicon production” and “feed preparation” steps. Nonetheless, Bolzano values could be combined with data on the missing steps from other sources to yield a more complete representation of the entire chain of producing virgin magnesium metal. For example, the same processing steps as the Pidgeon process should apply for the rest of the production chain. This could be done by adapting the Ramakrishnan and Koltun data to the Bolzano process and decreasing the ferrosilicon demand to 0.70 kg/kg-Mg and the dolomite demand to 10.6 kg/kg-Mg.

TABLE 2 Inputs to Bolzano (thermal) process for 1 kg magnesium ingot (Cherubini, 2008)

Step ID# ^a	Process Step	Output of Step	Diesel (liter)	Electricity (kWh)	Natural Gas (m3)
1	Mining/transportation ore	10.6 kg dolomite	0.006	0.358	–
5,6	Magnesium reduction	1 kg ingot	0.091	20.2	1.94
Totals			0.097	20.6	1.94

^a See Figure 1.

In a recent study conducted for the International Magnesium Association (IMA) by the German Aerospace Center (DLR, 2013), an updated analysis was conducted for both the thermal and electrolytic approaches for making magnesium. Results for the thermal process are given in Table 3. The values shown in the gas column of Table 3 represent processes using coke oven gas; data for those same processes using semi-coke oven gas, producer/generator gas, or natural gas were also given in that study, along with a weighted average value across manufacturers using the different gases.

TABLE 3 Inputs to the Pidgeon process for 1 kg of magnesium ingot (DLR, 2013)

Step ID# ^a	Process Step	Output of Step	Gas (m ³) ^b	Electricity (kWh)	Coke (kg)	Other Inputs
1	Mining	10.5 kg dolomite	–	–	–	–
2	Ore Prep & Calcining	–	2.6	0.192	–	–
3	Ferrosilicon production	1.05 kg (Fe)Si _x	–	8.92	1.05	1.19 kg quartz, 0.24 kg steel
4	Briquetting	–	–	0.672	–	0.13 kg CaF ₂ , 0.1 kg fluxes
5	Magnesium reduction	–	3.6	0.320	–	–
6,7	Ingot production	1 kg Mg ingot	0.6	0.049	–	–
Totals			6.8	10.16	1.05	

^a See Figure 1.

^b Coke oven gas case.

The DLR (2013) study purports to represent state-of-the-art operations making magnesium by using more efficient variants of processes evaluated earlier by other authors (Ramankrishnan & Koltun, 2002, 2004a, 2004b). The DLR data are derived from several sources: electricity production and coal mining from the Chinese LCI database, dolomite mining data fromecoinvent (2009), and Mg production process details, including energy reported by the Chinese Magnesium Association.

2.1.2 Electrolytic Production of Magnesium Metal

Electrolytic routes of magnesium production use resources from brine or ores. Electrolysis cells require very pure anhydrous magnesium chloride as input, so transformation and purification of the feed magnesium are important. U.S. Magnesium (USM) is the only company producing primary magnesium in the U.S., and it uses the electrolytic approach. The plant capacity was recently expanded from 50 kT to 63.5 kT annually (Kramer, 2012). However, because of the lack of available process detail for USM magnesium production operations, we start with data for the operations of an Australian Magnesium Corporation (AMC) plant. Unfortunately, due to the volatility of the magnesium market this plant never went into operation. Nevertheless, considerable process information has been published (Ramakrishnan and Koltun, 2002, 2004a) on that plant, and we expect its life cycle performance to be reasonably consistent with that of other electrolytic magnesium plants. A flow diagram of processes for electrolytic Mg production is shown in Figure 1.

During the past decade, AMC developed a process for electrolytic production of magnesium. It is based on the reaction of mined magnesite (MgCO₃) with HCl, where the produced MgCl₂ is subsequently dehydrated through a proprietary process to make feed suitable for electrolysis. Chlorine generated during electrolysis is directed to an onsite HCl production

unit. Make-up chlorine is supplied by electrolysis of NaCl, which coproduces NaOH. Hydrogen is supplied by reforming natural gas. A variety of chemicals is used in the unit processes; see Table 4 for a partial listing and Ramakrishnan and Koltun (2002) for more details. The fuels and energy used per kilogram of magnesium are given in Table 4. The two largest energy consumers are the electrolysis step, which uses 13 kWh/kg-Mg of electricity, and the dehydration step, which uses 28 kg of steam and 0.6 m³ of natural gas and 1.9 kWh/kg-Mg.

At USM operations, brine from the Great Salt Lake enters evaporation pools where 0.5 wt% Mg is concentrated to 9 wt%. Calcium chloride is added to precipitate sulfates, and long chain alcohols are used to extract boron compounds. Waste heat is used to preheat the concentrated brine before spray drying. Next, the spray dried powder is treated with chlorine and other reactants in melt reactors to remove heavy metals, water, and remaining MgO, sulfates, and bromine. The molten material is then transferred to the electrolytic cell.

Electrolysis cell conditions at USM include a temperature of 900°C and atmospheric pressure (Tripp, 2009). New electrolysis cells installed in 2002 lowered electrolysis electricity from 17.0 to 13.7 kWh/kg-Mg (Thayer & Neelameggham, 2001). Unfortunately, this value is currently the only available energy data for the Salt Lake USM operation. More information is required on the other steps in the USM process chain. For example, the facility produces chlorine gas and several chloride salts (iron, magnesium, calcium, and sodium). Because of this lack of life cycle information on the chlorine/chloride and other processes, our picture of the overall USM production scheme for Mg is incomplete.

TABLE 4 Inputs to AMC electrolytic process for 1 kg magnesium ingot (Ramakrishnan and Koltun, 2002, 2004a)

	Process Step	Output of Step	Electricity (kWh)	Natural Gas (m ³)	Diesel (liter)	Major Inputs
1	Mining, beneficiation	4.06 kg magnesite	0.013	–	0.023	–
2	Leaching	4.05 kg MgCl ₂	0.21	–	–	MgO, Cl ₂ , FeCl ₂ , H ₂ O, HCl
3	MgCl ₂ dehydration	–	1.93	0.60	–	C ₂ H ₆ O ₂ , CH ₃ OH, NH ₃ , 28 kg steam
4	Electrolysis	1 kg Mg	12.9	0.013	–	NaCl, CaCl ₂ , CaF ₂
7	Ingot production	1 kg Mg	0.288	0.043	–	–
6	HCl production	3.17 kg HCl	0.134	0.347	–	NaCl, Cl ₂
	Other ^a	–	0.985	–	–	–
	Overall energy		16.46	1.00	0.023	28 kg steam

^a Accounts for waste and water treatment, facilities, and utilities.

An early LCA of magnesium metal production was given by Albright and Haagensen (1997), who described the electrolytic approaches used for the Norsk Hydro plants. Those plants, one in Norway and the other in Quebec, are no longer in operation. Specific operational data were not given in the Albright and Haagensen paper on the various process steps. Nevertheless,

based on Kirk-Othmer (2010), the material flow for the Canadian plant is as follows: magnesite was reacted with HCl, yielding a brine that was subsequently treated with NaS, CaCl₂, and BaCl₂ to remove sulfates and heavy metals. The purified brine was next sent to prilling towers to form pellets of optimal size for dehydration to anhydrous MgCl₂ before being forwarded to the electrolytic cells. Albright and Haagensen (1997) presented only the CED of 144 MJ per kg of virgin Mg and did not provide any fuel consumption data. However, ecoinvent (2009) partitioned this CED value into hydroelectric and natural gas components. Taking their (ecoinvent, 2009) assumed percentages of total purchased energy as 60% hydroelectric and 40% natural gas, we calculated the following purchased energy values: 22 kWh of electricity and 1.44 m³ of natural gas, which yields a CED of 144 MJ/kg-Mg.

To assess the life-cycle performance of the AMC process, Cherubini et al. (2008) used data from Ramakrishnan and Koltun (2004a), a more abbreviated version of Ramakrishnan and Koltun (2002). For a kilogram of magnesium, 4.06 kg of magnesite is needed with 0.14 kWh of electricity to mine the ore, 3.07 kg of HCl for converting it to MgCl₂, and 0.004 m³ of natural gas for producing hydrogen for HCl production. For energy to the AMC process, 1.00 m³ of natural gas and 16.5 kWh of electricity are needed, which are similar to demands given by Ramakrishnan and Koltun (2004a). These data are summarized in Table 5. The energy results from Cherubini et al. (2008) are essentially the same as those in Table 4.

TABLE 5 Energy and material inputs to the AMC electrolytic process (extracted from Cherubini, et al., 2008) per kilogram magnesium ingot

	Process Step	Output of Step	Electricity (kWh)	Natural Gas (m ³)	Diesel (liter)
1	Mining ore and transportation	4.06 kg magnesite	0.14	–	0.004
3	MgCl ₂ dehydration	–	–	1.03	–
6	HCl production	3.07 kg HCl	0.002	0.004	–
4,7	Electrolysis	1 kg ingot	16.5	–	–
	Totals		16.7	1.034	0.004

The direct energy inputs for the production of a kilogram of magnesium in GREET2 are 30.4 kWh of electricity and 2.31 m³ of natural gas. However, these are legacy values from an earlier version of GREET2, and no information is available on what processes were considered.

Finally, DLR (2013) also evaluated the electrolytic approach for making magnesium. Unfortunately, the energy data they report for the electrolytic approach are not specific. For example, the energy needed for dehydration and chlorination is given as 54.4 MJ/kg-Mg, which for proprietary reasons is simply stated as a combination of coke, electricity, and natural gas. Four ores were considered though some, such as carnallite (KMgCl₃·6H₂O), are already a magnesium chloride salt, thus obviating the need for treatment with HCl. For the electrolysis step, DLR employs an energy value of 14 kWh/kg-Mg, which is reasonably consistent with those cited above.

2.1.3 Summary of Primary Production of Magnesium

Fuel consumption, CED, and GHG emission values for the references discussed above are summarized in Table 6. Notice the substantial variation among the references in the number of included process steps. For example, the USM process lists only electrolysis cell data with no information on the rest of the processes. By contrast, the data from the Pidgeon process (Ramakrishnan and Koltun, 2004b) and the AMC process (Ramakrishnan and Koltun, 2002) clearly represent more thorough analyses that account for all major magnesium production steps. From the results in Table 6, some initial comparisons and conclusions can be drawn.

The purchased energy (fuel) units for the various magnesium production processes given in Table 6 were taken from the above tables and references cited in them. Also given in the table are CED and GHG values that we calculated from those fuels using GREET1_2013. The units of CED and GHG are total primary energy consumed (MJ) and GHGs (kg of [CO₂]_{eq}) emitted per kilogram of virgin magnesium output, respectively. The GHG values include emissions from fuels and, where data are available (see table footnotes), ore-based CO₂ emissions. Differences between our CED and GHG values and those cited in original references are minor and attributed to differences in assumed grid electricity mix, transmission losses, and employed heating values between GREET values and those assumed in the original work. For example, CED and GHG values from Ramakrishnan and Koltun (2004a) for the Pidgeon process are 355 MJ and 42 kg of [CO₂]_{eq} per kg of Mg, respectively, which differ from our values in Table 6 by about 10%.

TABLE 6 Purchased energy units and corresponding CED and GHG values for producing a kilogram of virgin magnesium ingot via the electrolytic and thermal approaches.

Facility	Electricity (kWh)	Natural Gas (m ³)	Coal (kg)	Other	CED (MJ/kg) ^a	GHG (kg/kg) ^a	Included Steps
			Electrolytic				
USM	13.7	–	–		118	9.0	4
Norsk Hydro	22	1.44	–		237	17.2	3,4
AMC ^b	16.5	1.0	–	^c	308 ^d	25.5 ^d	1–7
GREET2_2012	30.5	2.31	–		357	25.7	unknown
			Thermal				
Pidgeon ^e	12.9	–	10.4	0.111 ^f	393	37.5 ^g	1-7
Bolzano ^h	20.6	1.94	–	0.097 ⁱ	196	9.3 ^j	1,5,6
Pidgeon ^k	10.16	6.8 ^l	1.05 ^m	–	256	30.3 ⁿ	1–7

^a Calculated (cradle to gate) using the U.S. grid average GREET (2012), unless stated otherwise. ^b From Table 4. ^c 28 kg of steam and 0.023 liters of diesel. ^d Assumed Australian grid mix and included 1.9 kg of CO₂ from ore in GHG value. ^e From Table 1. ^f Liters of diesel. ^g Includes 5.06 kg of ore derived CO₂ (Ramakrishnan & Koltun, 2004b). ^h From Table 2, Brazilian grid mix assumed. ⁱ Diesel. ^j Includes 1.27 kg of ore derived CO₂ (Cherubini, et al., 2008). ^k See Table 3, coke oven gas case (DLR, 2013). ^l Coke oven gas. ^m Coke. ⁿ 5.06 kg added from calcination of MgCO₃/CaCO₃.

Given the overall similarity in production process steps among electrolytic producers of Mg, the energy dominance of the electrolysis step, and the availability of life cycle data for all relevant process steps (Ramakrishnan and Koltun, 2002), we feel that the AMC data (see Table 6) are the most reliable and representative for the electrolytic production of magnesium, despite the plant having never been in operation. As seen in the table, data sets for plants with fewer processing steps included have, as expected, substantially lower CED and GHG values than those for AMC. Energy data for magnesium currently given in GREET2 are roughly comparable to the AMC data, but it is unclear just what processes are included. Due to the lack of specificity with regard to energy carriers, results from the DLR (2013) study for the electrolytic approach were not included in Table 6.

Of the thermal approach results given in Table 6, we consider the Pidgeon process data as the most reliable, primarily due to the inclusion of life cycle data for all relevant process steps. Both the Ramakrishnan and Koltun (2004b) and DLR (2013) studies provided substantial detail. The DLR values of CED and GHG shown in the table for the thermal route are lower than those estimated by Ramakrishnan and Koltun (2004b). The reasons for this discrepancy are not entirely clear but likely due to energy efficiency initiatives conducted by Chinese manufacturers. Given the wide variation in production process efficiencies typically encountered in life cycle studies, we conclude that these two Pidgeon process analyses represent a reasonable range of life cycle results (CED and GHG values) for the global production of magnesium. As seen in Table 6, the Bolzano CED and GHG values are much lower than their Pidgeon counterparts. This finding is attributed to some process differences between the two approaches, an ample supply of hydroelectricity in Brazil, and not all process steps being included in the analysis of the Bolzano approach.

2.2 COVER GAS AND GREENHOUSE GASES

Because the surface of the molten magnesium is sensitive to inclusions from oxidation, an inert blanket gas is generally used to protect the metal. Alternatively, sulfur powder is spread across the surface of molten magnesium for protection, as is common in the Pidgeon process. Historically, sulfur hexafluoride (SF_6) has been the preferred blanket gas, but it is an extremely potent greenhouse gas, with a global warming potential (GWP) of 23,900 $[\text{CO}_2]_{\text{eq}}$ per kg of gas (Sivertsen, et al., 2003). This burden is incurred during process operations where some of the gas is lost, having been emitted to the atmosphere; therefore, this gas must be made up. Alternatives to SF_6 as a cover gas have been a topic of research for over a decade. Two alternative gases being explored are SO_2 , which has no GWP but is both a criteria pollutant and corrosive, and HFC-134a, which has a GWP of 1,300 (Kramer, 2001). Use of HFC cover gas was planned for AMC operations (Ramakrishnan & Koltun, 2004a). From Ramakrishnan and Koltun (2002, 2004a, 2004b) and Cherubini et al. (2008), approximate consumptions of cover material per kilogram of pure Mg ingot have been estimated to be 1.1 g HFC-134a, 0.58 g SF_6 , and 0.05 kg S. Hence, cover gas fugitive emissions could add between 1.6 and 13.9 kg $[\text{CO}_2]_{\text{eq}}$ for HFC-134a and SF_6 , respectively, per kg of pure Mg ingot. There are no GHG emissions from using sulfur. In an effort to reduce GHG emission during magnesium (and part) production, blends of gases (such as HFC-134a/ CO_2 , SF_6 /air, and SO_2 /air) are being explored as potential cover gases (DLR, 2013). Though the use of SO_2 /air as a cover gas has the potential of acidification effects

and health impacts, its concentration is sufficiently low ($\approx 2\%$) to reduce its impact to tolerable levels, at least within the plants (DLR, 2013).

During the production of a magnesium auto parts, cover gases are also used when 1) casting magnesium ingots, 2) alloying the metal, and 3) molding or casting it into parts. Examples of SF₆ replacement rates for lost cover gas are given in Table 7; the three production stages covered are also included there. Replacement rate values by Reppe et al. (1998), Kiefer et al. (1998), and Tharumarajah and Koltun (2010) represent the sum of losses over all three stages, whereas the value by Albright and Haagensen (1997) covers only primary metal production. The Koltun et al. (2005) values apply only to the casting stage.

TABLE 7 SF₆ emission rates at various production stages per kilogram of magnesium

	g-SF₆ / kg-Mg in Part	Stages Covered
Reppe et al. (1998)	0.64	1 → 3
Kiefer et al. (1998)	1.23	1 → 3
Tharumarajah & Koltun (2010)	1.65	1 → 3
Albright & Hagensen (1997)	0.5	1
Koltun et al. (2005)	0.24	3

Clearly, the emission of SF₆ can be quite significant. For example, taking the first three values in Table 7, the equivalent GHG ranges from 15.3 to 39.4 kg [CO₂]_{eq} for a kilogram of magnesium parts. This range is equal to or greater than the values for producing the virgin metal in the first place, thereby effectively doubling the overall GHG emissions. Compared to sulfur powder, which has no GHG impacts, or HFC-134a, which only has 1.4 kg [CO₂]_{eq}/kg-Mg, it is obvious that significant greenhouse gas issues are associated with using SF₆. This finding provides motivation for SF₆ replacement.

2.3 SECONDARY PRODUCTION OF MAGNESIUM

Recycling of metals is critical to their overall sustainability. While production of metal goes from ore through intermediates, transportation, reactions, and purification before making the product, secondary production only needs to recover the functionality of the new product from the used product. Generally, the energy input is substantially lower, and the material inputs are sometimes negligible. In the U.S., 33% of magnesium metal (excluding aluminum alloys) comes from secondary production (Kramer, 2001). Magnesium retains most of the necessary physical integrity when recycled, as long as it is not contaminated. Remelting and forming of ingots are the main energy requirement for recycling. Albright and Haagensen (1997) report 1 kWh (3.6 MJ from hydroelectricity) per kg of recycled magnesium, whereas Kiefer et al. (1998) found 6 MJ per kg of recycled metals (fuel sources not given), including transport to/from the recycle center. Koltun et al. (2005) report energy requirements of 0.58 kWh and 1.29 ft³ natural gas per kg of recycled metal from recycled car parts.

Secondary production of Mg ingot requires substantially less energy than primary production. Caution must still be used in selecting a blanket gas, as the same amount of SF₆ is necessary for secondary casting to ingots as primary casting. For example, secondary ingot production releases a cumulative 3.6 kg [CO₂]_{eq}/kg-Mg (Tharumarajah & Koltun, 2007).

2.4 CASTING AND MOLDING

While the production of virgin magnesium is the majority of the total energy consumption for the corresponding finished product, the final product also uses processing energy for molding, casting, and finishing. Koltun et al. (2005) analyzed a converter housing made from a magnesium alloy. In this case, the ingot is melted for casting, with an electricity input of 0.53 kWh and natural gas demand of 0.02 m³ for 5.7 kg of magnesium. Casting, trimming, and finishing take 2.37 kWh of electricity to produce one converter housing of 3.1 kg magnesium; 2.5 kg of magnesium primary scrap flows back to closed loop recycling. Nominal energy is needed for auxiliary processes and installation of the part, as well as transportation.

Tharumarajah and Koltun (2007) analyzed the life cycle of an engine block made from magnesium alloy. The block was precision sand casted and had a final weight of 30 kg, 4 kg of which was steel liners. Melting the magnesium ingot consumed 3.64 kWh of electricity and 1.62 m³ of natural gas. Casting and finishing consumed 14.4 kWh of electricity. Energy inputs for sand molds and water treatment were also estimated. Electricity for sand molds was 8.39 kWh, and natural gas consumption was 1.84 m³.

Ramakrishnan et al. (2003) studied the life cycle of a converter housing. The manufacturing process consumed 22.76 MJ of direct energy: 33% to natural gas and 66% to electricity with 1% to diesel fuel. This converter housing weighed 3.6 kg and produced 3.95 kg of Mg scrap from the casting, trimming, and grinding processes. The energy demands are itemized in Table 8 using conversion factors and LHVs from GREET. Based on these three sets of purchased energy for Mg casting, their corresponding CEDs were computed and are also listed in Table 8. An inspection of the table reveals that all three values are in reasonable accord.

Shen et al. (1999) looked at the life cycle energy of a powertrain made via a novel magnesium molding process. This process involves chipping the magnesium, which can then be melted to form a molded part. This technology only incurs 31% waste, compared to more than 40% for die-cast or other molded parts. The fabrication step has an electricity input of 22.2 kWh per powertrain weighing 1.25 kg. This process, which is in the pilot stage of development, has an inordinately high casting energy compared to other casting processes, so it is not included in further discussion. To represent casting, we averaged the data in Table 8, which yielded 0.09 m³ of natural gas and 1.04 kWh per kg of magnesium in the product. The process average is 60.9% mass yield of product magnesium part per magnesium input.

TABLE 8 CED and GHG for molding/casting and finishing processes per kilogram of magnesium in part

	Natural Gas (m³/kg)	Electricity (kWh/kg)	CED (MJ/kg)	GHG (kg/kg)
Ramakrishnan et al. (2003)	0.06	1.2	13	1.0
Tharumarajah & Koltun (2007)	0.13	1.0	15	1.0
Koltun et al. (2005)	0.07	0.9	11	0.8

2.5 SUMMARY

While a great deal is known about the production of magnesium, additional data are still needed to complete the picture of primary magnesium production in the U.S. More specifically, information beyond just the electrolytic cell data for the USM operation would aid in this endeavor. Further, details on the hydrochloric acid production loop and cover-gas replacement rates also would be beneficial. This additional information would complete the picture of the process chain, from mining/ brine recovery to primary production of magnesium in the U.S.

For potential use in GREET, the Pidgeon (thermal) process data sets (Ramakrishnan & Koltun, 2002, 2004b; DLR, 2013) are the most complete. The processing steps can be summed to produce a full LCI for material and energy inputs. The calcium fluoride value likely needs revision, though it is probably not critical for most GREET LCI analyses. The AMC data set in Table 6 has enough detail to be used to represent electrolytic production of magnesium. Greenhouse gas emissions due to cover gas losses are substantial, and the values cited above appear to be reasonably representative of actual production. Koltun et al. (2005) provided the most detailed data on fuel use to represent the recycling of magnesium metal.

3 CARBON FIBER MARKET

According to the *Chemical Economics Handbook*, 9.3 kT of carbon fiber was produced in the U.S., and a net 2 kT more was imported in 2009 (Bizzari, et al., 2010). This carbon fiber represents about a third of the world consumption, and a quarter of the production. Three companies dominate the world production of carbon fiber: Toray, Toho Tenax, and Zoltek. The first two are Japanese companies that account for 41% of world carbon fiber capacity, about half of their capacity located in Japan. Zoltek is an American company, with a third of their production capacity in North America and the rest in Hungary.

Carbon fiber is a polymer treated at high temperatures (over 1000°C) to carbonize the material beyond 90% carbon content. Most carbon fiber production is integrated with the downstream processes, such as fabric and tape products. Carbon fibers are preferable over glass or natural fibers for reinforcing composites when higher tensile modulus is needed.

Carbon fiber is produced from several precursors, including rayon (from cellulose), polyacrylonitrile (PAN), or pitch (from petroleum). Other precursors are possible, but not widely used. Rayon was the first material commercially used for carbon fiber. This precursor is no longer manufactured in the U.S. and only used elsewhere for very high temperature applications due to its excellent thermal stability. The total world consumption of rayon-based carbon fiber is under 0.25 kT. Pitch is only used for aerospace applications and makes up 2.5% of the U.S. carbon fiber production capacity. Thus, PAN-based carbon fiber is the majority of the market and is the only precursor assessed in this report.

Carbon fiber is produced through a complex series of reactions and physical processes. A process block diagram of the PAN-based production pathway is shown in Figure 2. For more information on the processing steps, see Morgan (2005). Briefly, the production of carbon fiber is as follows. The starting materials for this process are natural gas and crude oil. Crude oil can be processed to many products, but propylene is the (distillation) fraction of interest for carbon fiber manufacture. In a separate process, natural gas is reformed with steam to produce hydrogen, which is subsequently reacted with nitrogen (from process air) to make ammonia. Propylene and ammonia react to form acrylonitrile, which is polymerized to form PAN with a small amount of co-monomer. PAN is typically spun into a fiber to align the molecules, which improves the structural performance of products made with these fibers. The acrylic fiber is oxidized in air and pyrolyzed in an inert gas above 1000°C to form carbon fiber.

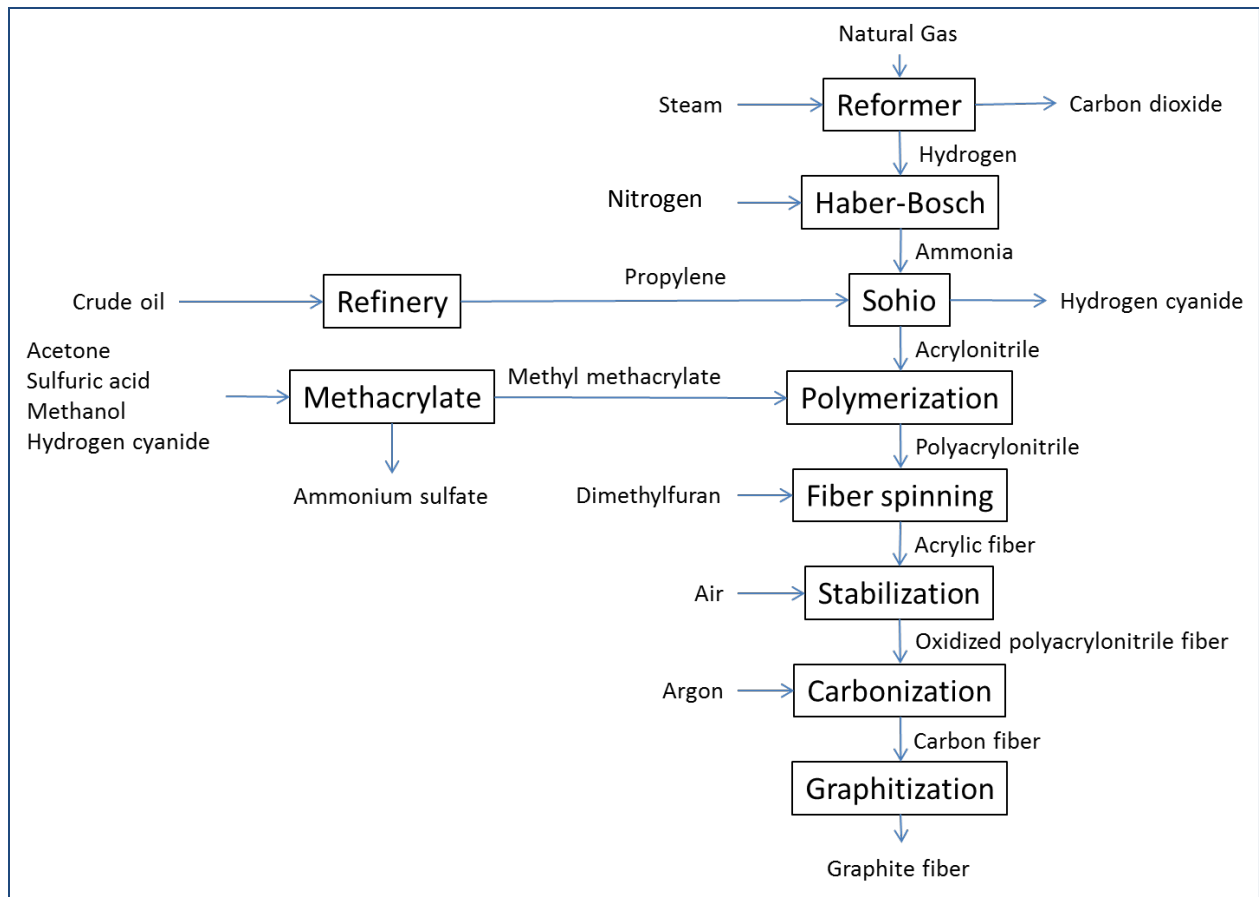


FIGURE 2 Process steps included in PCAs for producing carbon fibers

The breadth and depth of sources for the many process inputs are variable. We will analyze each processing step and product separately to highlight the quality of data available. The data sources represent U.S. and European operations, and the difference between the two sources can be significant. European industries tend to focus on improving energy efficiency to reduce resource use and cost more than in the U.S. For that reason, the geographic regions which data sources represent are also noted.

3.1 AMMONIA PRODUCTION

Ammonia production employs the Haber-Bosch process, wherein nitrogen and hydrogen react in the gas phase to form ammonia. The Fertilizer Institute (TFI) has surveyed production cost of fertilizer producers in North America. The response rate for ammonia producers is normally 75% of U.S. and Canadian capacity. For 1999, the weighted average value was 0.96 m³ natural gas/kg-ammonia (The Fertilizer Institute, 2000). The electricity demand averaged 0.13 kWh per kg of ammonia.

Jenssen and Kongshaug (2003) reference a benchmarking survey of natural gas consumption done by the Plant Surveys Institute. They found industry-average rates to be 0.98 m³ natural gas/kg-ammonia for European plants and 1.04 m³ natural gas/kg-ammonia for U.S. plants. The difference between the two demands is indicative of the better energy efficiency in the European industry.

The International Energy Agency (IEA) published a report called *Tracking Industrial Energy Efficiency and CO₂ Emissions*, which included ammonia as one of the chemical processes (IEA, 2007). That report estimated the natural gas consumption rate for U.S. ammonia plants to be 1.03 m³/kg-ammonia.

The United Nations Industrial Development Organization (UNIDO) published a 2010 report on industrial energy consumption. Their report contains survey data for worldwide production of ammonia from the International Fertilizer Association's 2007 benchmarks. The report shows that North American ammonia plants use 1.01 m³/kg-ammonia of natural gas (UNIDO, 2010).

The American Chemistry Council (ACC) Plastics Division sponsored a publication for the LCI of several polymers (Franklin Associates, 2011). Ammonia production was included in the inventory as a feedstock for polymers such as acrylonitrile. The ACC found the electricity demand for producing ammonia to be 0.14 kWh/kg of ammonia, which is in line with the TFI value, but the natural gas value is low by a factor of two. In fact, the ACC material flow of 0.418 kg of N₂ to make as stated in their report (Franklin Associates, 2011) a kilogram of NH₃ is clearly incorrect and actually represents both ammonia and co-produced CO₂. Because of uncertainties in ACC ammonia production outputs, we do not use their data on ammonia production.

To facilitate comparisons, Table 9 summarizes the reported total (feedstock and fuel) direct energy demands for ammonia production in U.S. plants via natural gas reforming processes. At the low end, natural gas consumption rates are 0.74 to 0.82 m³/kg-ammonia in new plants, whereas they are from 0.96 to 1.04 m³/kg-ammonia for currently operating plants, as shown in Table 9.

TABLE 9 Energy inputs for the production of a kilogram of ammonia in the U.S.

		TFI (2000)	Jenssen (2003)	IEA (2007)	UNIDO (2010)
Electricity	kWh	0.13			
Natural gas	m ³	0.96	1.04	1.03	1.01
CED	MJ	40.6	42.6	42.2	41.4
GHG	kg-[CO ₂] _{eq}	2.51	2.62	2.59	2.54

Based on the extensive surveys conducted by TFI on U.S. ammonia production, we use 0.96 m³ of natural gas and 0.13 kWh of electricity per kg of ammonia produced in the U.S. for our estimates of carbon fiber production given below.

3.2 PROPYLENE PRODUCTION

The second feedstock required for acrylonitrile production is propylene, which is a product of crude oil refining, often from the cracking of larger compounds. The ACC estimates the inputs for a kilogram of propylene to be 0.43 kg of crude oil, 0.20 kWh of electricity, and 1.08 m³ of natural gas, of which roughly 10% of the natural gas is process fuel (Franklin Associates, 2011). The diesel fuel demand for transportation is 6.81 x 10⁻⁴ liters/kg-propylene.

The Department of Energy (DOE) estimated the propylene process energy as 0.157 kWh and 0.071 m³ of natural gas per kg of propylene, based on mass allocation from the ethylene process that produces the propylene (Pellegrino, 2000). We assume that all the process heat was supplied by natural gas, rather than the generic fuel mixture that is assumed in the DOE report. These process energy demands are 1/3 lower than the 0.11 m³ of natural gas as fuel and 0.20 kWh of electricity from the ACC (Franklin Associates, 2011).

Plastics Europe is the industry association for European polymer manufacturers and has published numerous LCI reports for many polymers and their precursors (Boustead, 2005a,b,c). Values for propylene production are given in Table 10. Because of the way Plastics Europe organizes its data, the fossil fuels listed in the table include process and feedstock fuels as well as fuels burned to generate fossil-based electricity. The electricity listed in the table represents just the nuclear and hydro component.

The fuel inputs for propylene production are similar among the three sets of data shown in Table 10 in terms of CED. For our purposes here, we focus on the two U.S. entries, i.e., the ACC and U.S. LCI database (NREL, 2012) results, as the more appropriate representation of propylene production in the U.S.

TABLE 10 Purchased energy inputs for the production of a kilogram of propylene

		Boustead (2005a) ^a	Franklin Assoc. (2011)	NREL (2012)
Crude oil	kg	0.95	0.43	0.43
Natural gas	m ³	0.61	1.09	1.16
Electricity	kWh	0.33 ^b	0.20	0.15
Diesel	liters		6.81e-4	
Coal	kg	0.044		
Recovered energy ^c	MJ	-1.66		
CED	MJ	72.9	67.1	69.5
GHG ^d	kg-[CO ₂] _{eq}	4.69	4.26	4.40

^a All values in the reference were reported as kg and converted to units below. ^b Hydro and nuclear only. ^c Unspecified. ^d Includes CO₂ and other greenhouses where data available.

3.3 ACRYLONITRILE PRODUCTION

Acrylonitrile (AN) is made primarily from the Sohio process and consists of propylene, ammonia, and oxygen combining to form acrylonitrile and water at temperatures over 400°C (Sesto, et al., 2011). About 0.48 kg ammonia is needed per kilogram AN. Ullmann's *Encyclopedia* has a demand of one kilogram propylene feed to form 0.8-0.9 kg AN, with 0.02–0.11 kg acetonitrile and 0.15-0.2 kg HCN as byproducts (Langvard, 2002).

TABLE 11 Purchased energy inputs for the production of a kilogram of acrylonitrile

		Pellegrino (2000)	Neelis (2008)	NREL (2012)	Boustead (2005b) ^a
Natural gas	m ³	0.038	0.4	1.59	1.04
Coal	kg	0.014		0.215	0.093
Crude oil	kg	0.001		0.48	0.97
Electricity	kwh	0.111		0.048	0.49 ^b
Recovered Energy	MJ				-5.83
Ammonia	kg	0.48	0.48		
Propylene	kg	1.18	1.18		
CED	MJ/kg	2.9 ^c	1.6	94.3	95.9
GHG ^d	kg [CO ₂] _{eq} /kg	0.20 ^c	0.10 ^c	6.06	6.26

^a All values in the reference were reported as kg and converted to units below. ^b Hydro and nuclear electricity only. ^c Values estimated based on Tables 9 and 10 and natural gas listed above. ^d Includes CO₂ and other greenhouse gases where data are available.

Table 11 provides data on AN production energy and GHG results from four references. The two left-most entries detail only conversion processes starting with propylene and ammonia inputs. In her study, Pellegrino (2000) presented specific energy data corresponding to various fuels for a wide range of chemicals, including AN. As seen in the table, her results demonstrate that the process energy for AN is quite low. The Neelis et al. (2008) results also show this, though only the magnitude not the identity of process fuels was given in their study. The value in the table for Neelis et al. is based on our assumption that the fuel was natural gas. On the other hand, the U.S. LCI (NREL, 2012) and Boustead (2005b) values shown in Table 11 represent cradle-to-gate analyses for the production of a kilogram of AN. As a result, their CED and GHG values, which are in good accord with each other, are much higher than those of Pellegrino (2000) and Neelis et al. (2008). Because it was not feasible to separate out the process energy for AN production in the U.S. LCI (NREL, 2012) and Boustead (2005b) results, those values are not used in our estimation of carbon-fiber production energy and GHGs. Instead, we used the Pellegrino results, as they represent processing with substantial fuel detail.

3.4 POLYACRYLONITRILE PRODUCTION

Acrylonitrile serves as the main monomer unit in polyacrylonitrile (PAN). Polyacrylonitrile is normally manufactured by addition polymerization of AN with 10–15% co-monomers, such as methyl acrylate in solution to produce fibers that are 95% AN (Sesto & Mori, 2010). For our treatment we assume the co-monomer to be methyl methacrylate (MMA). Though others could be used, the co-monomer is only 5% of the fiber so its choice has minimal effect on the CED and GHG values for a kilogram of polymer.

Methyl methacrylate could use an entire analysis of its own to trace back its production from all primary processes, which is beyond the scope of this work. Instead of going to that level of detail, we use data from Plastics Europe, which reports the total energy requirements for the production of 1 kg of MMA to be 1.2 kWh of electricity, 0.93 kg of oil, 0.26 kg of coal, and 1.80 m³ of natural gas (Boustead, 2005c).

After the polymerization, the product is spun into fibers for the next stage of processing, which aligns the molecules in the chain. The molecular orientation is maintained when making carbon fiber and can enhance certain mechanical properties. The DOE estimated that the acrylic fiber production with suspension polymerization, filtration, drying, spinning, and finishing consumes 50.1 MJ/kg-PAN in process energy (1.45 kWh of electricity, 0.944 m³ of natural gas, 0.344 kg of coal, and 0.033 kg of crude oil per kg of PAN fiber) (Pellegrino, 2000).

Our PCA results for the production of a kilogram of PAN fibers are summarized in Table 12. The corresponding subtotals of required fuel values, denoted Pf1, were computed from the inner product of each fuel column with column 2. According to Das (2011), the full PCA to produce a kilogram of polymerized and spun PAN fibers, denoted Pf2, consumes 6.4 m³ of natural gas and 0.77 kWh of electricity. The Pf1 and Pf2 fuel values given in Table 12 show a considerable difference in the amount and types of fuels needed to produce a kilogram of PAN fibers. Further, the corresponding CED and GHG values for the Pf2 set are considerably higher than those for the Pf1 set. We have no explanation for this finding, other than that our PCA is

based on data from different sources and Das's (2011) fuel values are from a single source. Although Das (2011) did not provide details on each process step, his results are based on a recent communication with a composite producer. The different amounts and types of fuels between the Pf1 and Pf2 sets shown in Table 12 suggest that different process approaches with different energy efficiencies are being compared.

3.5 CARBON FIBER PRODUCTION

The remaining steps to produce carbon fiber (CF) involve heating PAN to 190–280°C to form oxidized polyacrylonitrile fiber (OPF), also called “stabilized acrylic,” which consists of 60% carbon and 9-14% oxygen (Linak, et al., 2011). This step cross-links the fibers and cyclizes the carbon structure, which prevents melting or burning in downstream processing. The OPF is subsequently heated to between 1000°C and 1700°C to deoxygenate the structure, forming 92–95% carbon-content fiber. The final step carbonizes the product to 99%+ carbon in the fiber. Energy values for these two steps can be found in Das (2011), where the oxidation step requires 2.67 m³ of natural gas (CED = 109 MJ) per kg of CF and 20.1 kWh (CED = 174 MJ) of electricity per kg of CF for carbonization. Heating oxidized fibers to temperatures above 2000°C produces graphite fibers, which are not considered in this analysis.

3.6 CUMULATIVE ENERGY DEMAND AND GHG EMISSIONS FOR CF PRODUCTION

Table 12 summarizes the cradle-to-gate CED and GHG values for the production of carbon fibers. The data show that our Pf1&CF estimated fuel values yield lower CED and GHG values (632 MJ/kg and 42.5 kg/kg, respectively) than those of the Pf2&CF set. As both sets of CED and GHG values use the same fiber oxidation and carbonization data, the differences arise from differences between the fuels detailed in our PCA of PAN fiber production (Pf1) and those from Das (2011). As in Das (2011), we assumed that 2.08 kg of PAN fibers is required to make a kilogram of CF. The energy inputs for oxidation and carbonization processes contribute around 45% and 34%, respectively, of the Pf1&CF and Pf2&CF sets.

The literature gives a great variety of energy values for the fuels required to make carbon fibers. For example, DeVegt and Haije (1997) estimated the carbonization energy to be 2.52 MJ/kg-CF. Given the temperatures cited above for carbonization, their values are clearly inordinately low. Much higher values have been published by others: 286 MJ/kg by Susuki and Takahashi (2005), and 460 MJ/kg by Takahashi et al. (2002). Van Acker et al. (2009) cite two values: 186 MJ/kg and 364 MJ/kg. Unfortunately, these references provide very little to no information on just what steps in the CF process chain are included in the estimates.

TABLE 12 Materials, fuels, CED, and GHG for the production of a kilogram of carbon fiber (CF) from PAN fibers from our PCA data from Das (2011)

Process	Input to Next Step (kg)	Fuel Rates Per Unit Input			
		Natural Gas (m ³ /kg)	Electricity (kWh/kg)	Coal (kg/kg)	Oil (kg/kg)
NH ₃ Production ^a	0.456	0.96	0.13	–	–
C ₃ H ₆ Production ^b	1.116	1.16	0.15	–	0.43
Acrylonitrile ^c	0.95	0.038	0.111	0.014	0.001
MMA	0.05	1.80	1.2	0.26	0.93
PAN fibers ^d	1	0.944	1.45	0.344	0.033
Pf1 Subtotal	2.08 ^e	2.80	1.84	0.37	0.56
Pf2 ^f Subtotal	2.08 ^e	6.36	0.77	–	–
CF ^{f,g}	1	2.67 ^f	20.1 ^f	–	–
		PAN		CF	
		CED (MJ/kg)	GHG (kg/kg)	CED (MJ/kg)	GHG (kg/kg)
	Pf1 & CF ^f	350	22.7	632	42.5
	Pf2 & CF ^f	557	34.4	840	54.2

^a Haber-Bosch process. ^b From refinery. ^c SOHIO process. ^d Polymerization of propylene, acrylonitrile, and MMA and subsequent PAN fiber production. ^e Need 2.08 kg of PAN fibers to make 1 kg of CF. ^f From Das, 2011.

^g PAN oxidation and carbonization to CF.

Due to substantially more process detail, we feel that the Pf1&CF data set for fuel, CED, and GHG values best represents the production of carbon fibers via the PAN route. However, additional detailed LCA studies for the production of CF are desirable, especially considering that process efficiencies tend to increase over time.

To make carbon fiber composites, fibers are typically braided or woven into a cloth. However, the energy for weaving was not considered in this report. Because it is typically small compared to the other processing steps to produce the fiber (Duflou, et al., 2009), we do not expect this energy demand to affect the CED much. Also, we have not considered the end-of-life treatment of the carbon fiber/composite. At the end of the useful life of the product, the carbon fiber composite will have sub-standard mechanical performance. It is difficult to recycle composites, although this option may be possible in the future. One consideration from a life cycle perspective is to recover some of the energy content of the polymer by burning or pyrolyzing it (Witik, et al., 2013). This would allow for recovery of the energy in a useful form; thus, the CED value could get a credit for the heat energy produced, depending on the life-cycle allocation approach assumed by the analyst.

4 CONCLUSION

Based on a literature survey, cradle-to-gate LCI data have been developed for making carbon fibers and magnesium. These materials can be used for lightweighting applications on cars and trucks, thus improving their operational efficiency; however, updated life-cycle data for the production of carbon fiber and magnesium are needed to better assess their impact on the life-cycle environmental performance of those vehicles. The LCA approach used is PCA, which was applied to two production routes for magnesium, thermal and electrolytic. In both cases, references were found from which adequately detailed life cycle data were compiled for representing up-to-date energy and emissions production data for thermally and electrolytically produced magnesium. Globally, magnesium is mostly produced in China through the Pidgeon process, which is a thermal route that has been adequately described for life cycle purposes in several publications. For the electrolytic approach of making magnesium, the most complete life cycle data were found in Australian publications for a plant that never went into operation in that country. However, because those data are substantially detailed, they are deemed representative of the electrolytic production route. Unfortunately, no data of sufficient quality were found for U.S. electrolytic magnesium production.

Carbon-fiber production data for all relevant stages of its PCA were also discussed. A number of studies were found to provide adequate life cycle detail on the production processes for key precursors of carbon fibers, namely, propylene, ammonia, and acrylonitrile. However, fewer studies were found to present adequate detail on production of PAN fibers and their subsequent oxidation and carbonization to carbon fibers. Nonetheless, from studies that were available, we have developed a complete PCA for carbon fiber production that provides a reasonable estimate of the life cycle performance of carbon fibers in terms of CED and GHG values.

Given the quality and quantity of process detail, we feel that the cradle-to-gate data sets developed herein are suitable updates for the data that currently reside in GREET2 for these materials.

This page intentionally blank.

5 REFERENCES

- Albright, D. & Haagenen, J., 1997. Life cycle inventory of magnesium. Toronto, World Magnesium Conference.
- Bizzari, S., Kalin, T. & Yokose, K., 2010. Carbon fibers. In: *Chemical Economics Handbook Marketing Research Report*. Menlo Park, CA: SRI Consulting.
- Boustead, I., 2005a. Eco-profiles for the European Plastics Industry: Propylene. Brussels: Plastics Europe.
- Boustead, I., 2005b. Eco-profiles for the European Plastics Industry: Acrylonitrile. Brussels: Plastics Europe.
- Boustead, I., 2005c. Eco-profiles for the European Plastics Industry: Methyl Methacrylate. Brussels: Plastics Europe.
- Cherubini, F., Raugei, M. & Ulgiati, S., 2008. LCA of magnesium production. *Resources, Conservation, and Recycling*, Volume 52, pp. 1093–1100.
- Das, S., 2011. Life cycle assessment of carbon fiber-reinforced polymer composites. *International Journal of Life Cycle Assessment*, Volume 16, pp. 268–282.
- De Vegt, O. & Haije, W., 1997. *Comparative Environmental Life Cycle Assessment of Composite Materials*. The Netherlands: European Commission Network (ECN).
- DLR, 2013. *Life Cycle Assessment of Magnesium Components in Vehicle Construction*. German Aerospace Center, www.intlmag.org/newsroom/2013IMA_LCAStudy_Summary.pdf, accessed 4/21/2014.
- Duflou, J., De Moor, J., Verpoest, I. & Dewulf, W., 2009. Environmental impact analysis of composite use in car manufacturing. *CIRP Annals: Manufacturing Technology*, Volume 58, pp. 9–12.
- ecoinvent, 2009. *Life Cycle Inventories for Metals*. Volume 2.1, Report No. 10, <http://www.ecoinvent.org/management@ecoinvent.org>, accessed 5/15/2014.
- Franklin Associates, 2011. Cradle-to-Gate Life Cycle Inventory for Nine Plastic Resins and Four Polyurethane Precursors. Plastics Division of the American Chemistry Council.
- Gao, F., et al., 2008. Assessing environmental impact of magnesium production using Pidgeon process in China. *Transactions of the Nonferrous Metal Society of China*, Volume 18, pp. 749–754.

- GREET1 and GREET2, 2012. *Greenhouse Gases, Regulated Emissions and Energy in Transportation (GREET) Model*. Argonne National Laboratory, http://greet.es.anl.gov/greet_1_series, accessed July 31, 2012.
- IEA, 2007. *Tracking Industrial Energy Efficiency and CO₂ Emissions*. Paris: International Energy Agency.
- Jenssen, T. K. & Kongshaug, G., 2003. *Energy Consumption and Greenhouse Gas Emissions in Fertilizer Production*. London: International Fertilizer Society.
- Kiefer, B., Deinzer, G., Haagensen, J. & Saur, K., 1998. Life cycle engineering study of automotive structural parts made of steel and magnesium. SAE technical paper series, No. 982225.
- Kirk-Othmer, 2010. Magnesium and magnesium alloys. In: *Encyclopedia of Chemical Technology*, Wiley, pp. 1–55.
- Koltun, P., Tharumarajah, A. & Ramakrishnan, S., 2005. Life cycle environmental impact of magnesium automotive components. In: N. Neelameggham, H. Kaplan & B. Powell, eds., *Magnesium Technology*, TMS, pp. 43–48.
- Kramer, D., 2001. *Magnesium Recycling in the United States in 1998*. Reston, VA: United States Geological Survey Report 01-166.
- Kramer, D., 2010. Magnesium. In: *Mineral Yearbook*. Reston, VA: United States Geological Survey.
- Kramer, D., 2012. *Mineral Commodity Summaries: Magnesium*. Reston, VA: United States Geological Survey.
- Langvard, P., 2002. *Ullmann's Encyclopedia of Industrial Chemistry*. Weinheim, Germany: Wiley-VCH.
- Linak, E., Blagoev, M., Kumamoto, T. & Xiaoxiong, H., 2011. Specialty organic fibers. In: *Chemical Economics Handbook Marketing Research Report*. Menlo Park: SRI Consulting.
- Morgan, P., 2005. *Carbon Fibers and Their Composites*. Boca Raton: Taylor and Francis.
- Neelis, M., Worrell, E. & Masanet, E., 2008. *Energy Efficiency Improvement and Cost Savings Opportunities for the Petrochemical Industry*. Berkeley, CA: Lawrence Berkeley National Laboratory.
- NREL, 2012. *U.S. LCI Database*, www.nrel.gov/lci, accessed 5/15/2014.

- Pellegrino, J., 2000. *Energy and Environmental Profile of the U.S. Chemical Industry*. Washington, D.C.: U.S. Department of Energy, <http://www.energy.gov/eere/amo/downloads/itp-chemicals-energy-and-environmental-profile-us-chemical-industry-may-2000>.
- Ramakrishnan, S., & Koltun, P., 2002. Life cycle analysis of Australian magnesium ingots. Stage 1: Cradle to Cast-house Gate LCI Analysis. CSIRO Manufacturing Science and Technology, Preston, Vic 3072, Project MP0045.
- Ramakrishnan, S., & Koltun, P., 2004a. A comparison of the greenhouse impacts of magnesium produced by electrolytic and pidgeon processes. In *Magnesium Technology*, A. Luo, ed., TMS, pp. 173–178.
- Ramakrishnan, S., & Koltun, P., 2004b. Global warming impact of the magnesium produced in China using the Pidgeon process. *Resources, Conservation, and Recycling*, Volume 42, pp. 49–64.
- Ramakrishnan, S., Tharumarajah, A., Koltun, P. & Roberts, M., 2003. Eco-efficient light metals component manufacturing. Brisbane, International Light Metals Technology Conference.
- Reppe, P., Keoleian, G., Messick, R. & Costic, M., 1998. Life cycle assessment of a transmission case. SAE Technical Paper Series, No. 980470.
- Sesto, B., Kumamoto, T. & Giacobbe, G., 2011. Acrylonitrile. In: *Chemical Economics Handbook Marketing Research Report*. Menlo Park, CA: SRI Consulting.
- Sesto, B. & Mori, H., 2010. Acrylic and modacrylic fibers. In: *Chemical Economics Handbook Marketing Research Report*. Menlo Park, CA: SRI Consulting.
- Shen, D., Phipps, A., Keoleian, G. & Messick, R., 1999. Life cycle assessment of a powertrain structural component. SAE technical paper series, No. 1999-01-0016.
- Sivertsen, L., Haagenen, J. & Albright, D., 2003. A review of the life cycle environmental performance of automotive magnesium. SAE Technical Paper series, No. 2003-01-0641.
- Suzuki, T. & Takahashi, J., 2005. Prediction of energy intensity of carbon fiber reinforced plastics for mass-produced passenger cars. 9th International SAMPE Symposium.
- Takahashi, J., et al., 2002. Life cycle assessment of ultra lightweight vehicles using CFRP. Tsukuba, Japan, 5th International Conference on EcoBalance.
- Tharumarajah, A. & Koltun, P., 2007. Is there an environmental advantage of using magnesium components for light-weighting cars, *Journal of Cleaner Production*, Volume 15, pp. 1007–1013.
- Tharumarajah, A. & Koltun, P., 2010. Improving environmental performance of magnesium instrument panels. *Resources, Conservation, and Recycling*, Volume 54, pp. 1189–1195.

Thayer, R. & Neelameggham, R., 2001. Improving the electrolytic process for magnesium production. *JOM*, Volume 53, pp. 15–17.

The Fertilizer Institute, 2000. *Production Cost Surveys*. Muscle Shoals, AL: International Fertilizer Development Center.

Tripp, T., 2009. Production of magnesium from Great Salt Lake, Utah. *Natural Resources and Environmental Issues*, Volume 15, Number 10.

USGS, 2013. *Minerals Information: Magnesium*, <http://minerals.usgs.gov/minerals/pubs/commodity/magnesium>, accessed 5/15/2014.

U.S. Magnesium LLC, 2011. *Cogeneration*, <http://usmagnesium.com/environment/cogeneration>, accessed 10/07/2012.

UNIDO, 2010. *Global Industrial Energy Efficiency Benchmarking*. United Nations Industrial Development Organization.

Van Acker, K., Verpoest, I.D.M.J., Duflou, J. & Dewulf, W., 2009. Lightweight materials for the automotive: Environmental impact analysis of the use of composites. Freiberg, 3rd Seminar on Society and Materials SAM3.

Witik, R., Teuscher, R., Michaud, V., Ludwig, C., Manson, J. 2013. Carbon Fibre reinforced composite waste: An environmental assessment of recycling, energy recovery, and landfilling. *Composites: Part A*, Volume 49, pp. 89–99.

Wulandari, W., Brooks, G., Rhamdhani, M. & Monaghan, B., 2010. Magnesium: Current and alternative production routes. Adelaide, Chemeca, Australasian Conference on Chemical Engineering.



Energy Systems Division

9700 South Cass Avenue, Bldg. 362
Argonne, IL 60439-4815

www.anl.gov



Argonne National Laboratory is a U.S. Department of Energy
laboratory managed by UChicago Argonne, LLC