



Final Technical Report

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Final Scientific/Technical Report

Scale-up of Novel Low-Cost Carbon Fibers Leading to High-Volume Commercial Launch

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List of Acronyms

Air conditioning and heating units	AHU
Advanced Manufacturing Office	AMO
Barrels per day	bpd
Carbon Fiber	CF
Carbon Fiber Technology Facility	CFTF
Collaborative Research and Development Agreement	CRADA
Critical to quality	CTQ
Dimethylacetamide	DMAC
Dimethylformamide	DMF
High density polyethylene	HDPE
Linear low density polyethylene	LDPE
Mechanical refrigeration units	MRU
Michigan Economic Development Corporation	MEDC
Oak Ridge National Laboratory	ORNL
Polyacrylonitrile	PAN
Polyolefin	PO
Project Management Plan	PMP



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Executive Summary

The project started in September, 2012 with the goal of scaling up from the existing laboratory scale process for producing carbon fiber (CF) from polyolefin (PO) based precursor fiber using a Dow proprietary sulfonation-desulfonation stabilization process. The award was used to develop a process that was capable of producing market development quantities of CF from PO precursor fiber at a rate of 4 kg/h of CF. The CF would target properties that met or exceeded the Department of Energy (DOE) Vehicles Technology [1] standard; i.e., 172 GPa modulus and 1.72 GPa strength at greater than or equal to 1% strain. The Dow proprietary process was capable of meeting and exceeding these targets properties. Project DE-EE0005760 resulted from a Collaborative Research and Development Agreement (CRADA) between Dow and Oak Ridge National Laboratory (ORNL) with support from the Michigan Economic Development Corporation (MEDC) and DOE.

In the first budget period, the main goal was to design a sulfonation-desulfonation market development plant capable of stabilizing PO precursor fiber at a rate of 5 kg/h using a sulfonation solution. The detailed design, location, and cost estimate were determined as scheduled in the Project Management Plan (PMP). In parallel with this DOE award project was a fundamentals and economic evaluation funded by The Dow Chemical Company (Dow). The goal of the Dow sponsored project was to finalize the mass balances, energy balances, and levelized cost to produce CF using the Dow process. A Go-No-Go decision was scheduled in June, 2013 based on the findings of the DOE sponsored scale up project and the Dow sponsored project.

In June, 2013, Dow made the No-Go decision to halt and abandon the Dow proprietary sulfonation-desulfonation process for stabilizing PO precursor fibers for the manufacturing of CF. This No-Go decision was identified in the original proposal and at the start of this project, and the decision was made as scheduled. The decision was based on the high levelized economic cost of the process relative to the manufacture of CF from polyacrylonitrile (PAN) precursor fibers. The capital required to sulfonate the fibers adds a significant cost to the process due to the need for investment in a sulfuric acid recovery plant. This high additional capital over the capital for a PAN based CF plant, reduces the levelized economic cost to slightly advantaged over PAN based CF. The sulfonation-desulfonation stabilization route failed to meet the Dow's return on investment criterion and the cost advantage target set forth for the DOE project.

The DOE and Dow decided to halt spending on the project until a new PO fiber stabilization process could be identified that met the DOE physical properties standard and the levelized economic cost constraints of Dow. When the new technology was developed, then award DE-EE0005760 would be re-started with the same goals of the development of a market development plant capable of producing CF at 4 kg/h with the properties that met or exceed those set forth by the Department of Energy Vehicles Technology standard. Progress on the development of the new process has been slow and thus has delayed the scale up project.

Dow's efforts to date have not progressed to the point of demonstrating a commercially-viable process for production of low cost CF from PO precursors for Dow's rigorous economic constraints. After extensive discussions within Dow and consultation with DOE's Advanced Manufacturing Office (AMO) Headquarters and Golden Field Office teams, Dow has decided to proceed with the formal recommendation to terminate subject project. DOE's AMO Headquarters and Golden Field Office teams agreed with the termination of the project.



Introduction

The high cost of carbon fiber (CF) from polyacrylonitrile (PAN) precursor fiber limits their use to defense and aerospace applications. Production of industrial CF from polyolefin (PO) precursor fibers has the potential to decrease the cost and increase the availability of CF, allowing its use in industrial applications such as automotive and wind energy systems. To date, CFs have been produced successfully from PO precursors only at the laboratory scale. The goal of this project is to produce market development quantities of CF from PO precursor at a rate of 4 kg/h of finished CF product with properties that are set forth by the Department of Energy Vehicles Technology [1] standard; i.e., 172 GPa modulus and 1.72 GPa strength at greater than or equal to 1% strain. The demonstration will produce 800 kg of finished CF. Post treatment of the fiber and evaluation in composite test specimens will be performed once CF is available. Precursor formulation and process development is ongoing with a Collaborative Research and Development Agreement (CRADA) at the lab scale. The intent of this project was to scale up these results. The specific project objectives are as follows:

- Operation of a 4 kg/h carbonization and post treatment plant at ORNL's Carbon Fiber Technology Facility (CFTF).
- Scale up of the Dow proprietary sulfonation-desulfonation process to a rate of 4 kg/h CF.
- Identification and application of acceptable post treatments.
- Production of 800 kg of CF from PO precursors with properties that meet the Department of Energy Vehicles Technology [1] standard.
- Validation of the CF quality in composite test specimens.

The scope of this project is to develop a market development scale process capable of producing low cost CFs from PO precursor fiber at rates of 4 kg/h of finished CF. The scope includes the scale-up of the melt spinning of PO fibers using the Dow melt spinning plant (Midland), the sulfonation-desulfonation of the PO fibers in the Dow Market Development plant, and the carbonization of the desulfonated fibers at ORNL's CFTF followed by post treatment at the CFTF. Two lots of 400 kg each (800 kg total) of CF from PO precursors will be produced with properties that meet or exceed the Department of Energy Vehicles Technology standard [1]. The post-treated CFs produced will be evaluated in composite test specimens and subject to customer critical to quality (CTQ) parameters. These include testing of the modulus and strength of the CF, adhesion to matrix resins, physical properties of composite test specimens, durability, and fastening to other materials.

The scale-up research and design for "Scale-up of Novel Low-Cost Carbon Fibers Leading to High-Volume Commercial Launch is partially funded by the Department of Energy (DOE) under award number DE-EE0005760. The award was for \$9MM with a 33% cost share (total project funded at \$13.5MM), and it started on September 1, 2012 and is scheduled to end February 28, 2016. ORNL and Ford Motor Company (Ford) are co-collaborators, with ORNL providing access to the Pilot Line and the CFTF and Ford providing research in composite development and testing. Dow will be responsible for the overall direction of the project, melt spinning the PO fibers, sulfonation-desulfonation of the PO fibers, and fiber testing.

This paper documents the progress and key learnings up to the joint decision by Dow and the DOE to terminate program DE-EE0005760. The decision to terminate was based on the high level of capital required to sulfonate the fibers. This capital adds a significant cost to the process due to the need for investment in a sulfuric acid recovery plant. This high additional capital over the capital for a PAN based CF plant, reduces the levelized economic cost to slightly advantaged over PAN based CF. The sulfonation-desulfonation stabilization route failed to meet the Dow's return on investment criterion and the cost advantage target set forth for the DOE project.

Background

Polyolefin-based CFs offer significant cost benefits through high mass yield, low raw material cost (compared to PAN), ease of precursor handling, and processability. PO precursors may also offer improved performance properties specific to non-aerospace applications such as ground transportation and wind turbines than those that are achievable with other low-cost CF precursors, such as lignin, by extending the physical property of elongation to break from less than 1.0% to greater than 1.5%. Therefore, carbon fibers derived from PO precursors could provide significant value in terms of performance-to-cost ratio versus other identifiable precursor candidates that are being considered for low-cost CF. Polyolefin based precursor fibers are melt spun using traditional fiber spinning processes [2,3]. The fibers are then treated using a Dow proprietary process to form stabilized precursor fibers for subsequent carbonization. About 1.4 kg of a low-cost PO resin is required to produce 1 kg of CF. As a comparison it takes about 2 kg of a high-cost PAN resin to produce 1 kg of CF.

Precursor PO fibers are produced using a traditional melt spinning extrusion process [2,3]. For this process, the PO resin in pellet form is fed to a single-screw extruder [4], melted, and then pumped to a spinning die. The fibers are pulled into a tow and stretched to the desired diameter. The PO precursor fiber is then sulfonated using a Dow proprietary process. This sulfonation process causes the PO polymer to become thermally set and removes many of the hydrogen atoms from the PO molecule. Next, the fiber is thermally desulfonated, forming fibers that are carbonized but not in the proper molecular configuration.

The desulfonated fibers are carbonized to high-strength CFs using a high-temperature process. The fiber is post-treated (surface treated and sized) downstream from the high-temperature furnace and then wound onto rolls. The process is shown schematically in Figure 1.

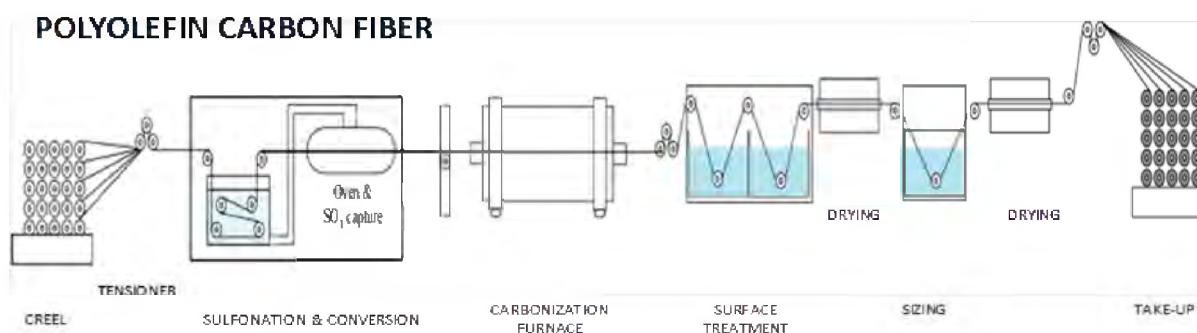


Figure 1. Schematic of the process used to carbonize PO precursor fiber into carbon fiber.

Currently, much of the commercial CF supply is produced from PAN precursor fibers. This route is expensive due to the high cost of PAN resin, the cost to solution spin the PAN resin, and the low yield of the process (~50%). Cost analysis by Dow indicates that the PAN resin and its preparation into precursor fiber accounts for about half the cost to manufacture CF. To produce the PAN precursor fiber [5], the PAN resin is first dissolved in a mixture containing either dimethylformamide (DMF, for dry spinning) or dimethylacetamide (DMAC, for wet spinning). Next the PAN solution is forced through a spinneret die with many small diameter holes. For dry spinning, the spinneret produces fibers that are then treated in air to remove the solvent. For wet spinning, the fiber tow is pulled through a bath where the solvent is extracted from the PAN solution. The PAN precursor fibers are then wound onto rolls. The PAN precursor fiber is passed through an oxidation oven with typically four temperature zones. The zone temperatures progressively increase with the final zone temperature near 250°C. The total residence time is between 2 and 4 hours [2]. Due to the high level of hydrogen bonding between the PAN chains, the fibers maintain their structure through the process. The downstream sections of the PAN and PO processes are very similar in that the oxidized PAN fiber is pulled through a high temperature furnace, surface treated, and then sized. A schematic of the PAN process is shown in Figure 2.

PAN CARBON FIBER

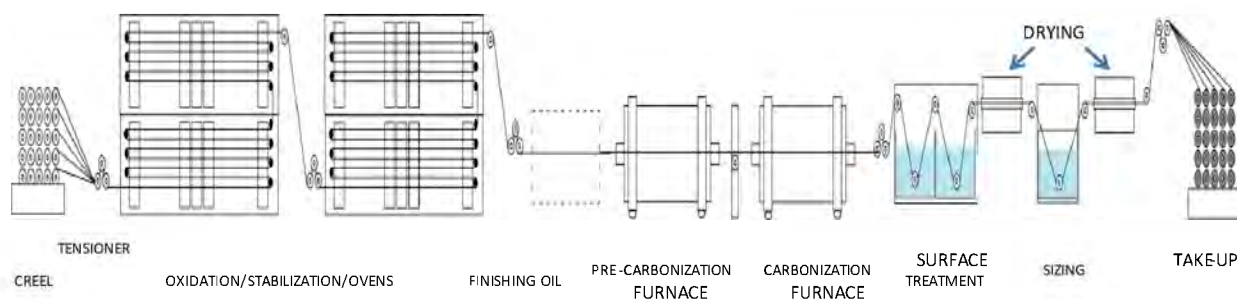


Figure 2. Schematic of the process used to carbonize PAN precursor fiber into carbon fiber.

The key technology section for converting PO precursor fiber to CF was the Dow proprietary sulfonation-desulfonation process. Horikiri, Iseki, and Minobe [6] of Sumitomo Chemical, Limited were the first to produce CF from high density polyethylene (HDPE) fiber using a sulfonation-dehydration process. The Sumitomo Chemical team was able to produce a sample CF with a modulus of 147 GPa and a strength of 2.3 GPa. This was followed by work in academia by Posterna and Penning [7,8]. They used a linear low density polyethylene (LDPE) to produce CF with a modulus of 130 GPa and a strength of 2.0 GPa. Zhang at The University of Tennessee in 1996 was able to make CF samples with a modulus of 200 GPa and a strength of 2.0 GPa using ultrahigh molecular weight, highly drawn polyethylene fiber [9,10]. Although this fiber exceeded the Department of Energy Vehicles Technology [1] standard, the fiber did not have properties for the target aerospace industry and the effort was abandoned. The Dow proprietary process has consistently produced CFs with properties that exceed the Department of Energy Vehicles Technology [1] standard at a lab scale rate of 0.3 g/h.

The Scale Up Project

The ultimate goal of project DE-EE0005760 was to scale the lab process at a rate of 0.3 g/h to a market development rate of 4 kg/h. For the market development rate, the PO precursor fibers would be melt spun using a fiber spinning line in Dow Midland and wound onto rolls. The spinning line in Midland exists and would only need minor modifications to spin fibers at the



required rate. These fibers would then be combined into 6k (6000 fibers) tows and rewound onto rolls. At the sulfonation-desulfonation market development line, four of these 6k tows would be combined and then passed through the process. At the end of the process, the 24k desulfonated and stabilized tow would be wound back onto rolls. The market development line was not designed or built at the start of the project. This sulfonation-desulfonation line would be built at Dow's cost and located in Midland, MI. The 24k stabilized tows would be shipped to ORNL. ORNL would pass these tows through the high temperature furnaces, surface treatment equipment, and sizing equipment at the CFTF. The rate out of the process was targeted at 4 kg/h with CF properties meeting or exceeding the Department of Energy Vehicles Technology [1] standard. The resulting CF would be shipped to Dow and also to Ford for evaluation. The project was divided into three budget periods with the final goal of producing 800 kg of CF at a rate of 4 kg/h that met or exceeded the Department of Energy Vehicles Technology [1] standard in budget period 3.

During the first budget period, the main goals were to get the Pilot line at ORNL ready for process development in budget period 2, produce 300 m long 3k tows of sulfonated-desulfonated fiber using the Dow lab lines, design and obtain a cost estimate for building the market development line for sulfonation-desulfonation. Near the middle of the first budget period, Dow will decide whether to build a market development scale sulfonation-desulfonation plant. The Dow internal decision will be based on a risk assessment, the capital cost of the equipment, risks associated with safe operation, and the economic evaluation for the process.

During the second budget period, the main goals were to build the sulfonation-desulfonation market development line at Dow and at Dow's cost, use the pilot line at ORNL to obtain processing ranges for the CFTF so that CF can be produced that meets or exceeds the Department of Energy Vehicles Technology [1] standard, and prepare for operation of the CFTF at 4 kg/h CF.

The sulfonation-desulfonation market development plant was scheduled to be operational by the start of budget period three. The main goals of budget period three were to produce two lots of 400 kg CF each at a rate of 4 kg/h that met or exceeded the Department of Energy Vehicles Technology [1] standard and the evaluation of the physical properties of the CF and composite test samples.

Results and Discussion

The process to produce CF from PO precursor fibers is a Dow proprietary process and as such cannot be disclosed here. The scale up technology will be discussed in general terms such that the Dow proprietary technology is not disclosed. Scale up results exist only for the first half of the first budget period; i.e., up to the time that the project was halted by Dow. During this time period the Dow sponsored process development project was optimizing the process conditions and feedstock demands. The next sections will discuss the scaled up process for production of the precursor PO fiber, tow combining, and sulfonation-desulfonation process. The process rate of 4 kg/h was set based on the capability of the furnaces and downstream equipment at the CFTF at ORNL. Because the CFTF could operate at the required rate, no modifications to the CFTF were warranted at this time.

Scale Up of the Melt Spinning Process

In order to produce CF at a rate of 4 kg/h, PO precursor fiber must be produced at a rate of 5 kg/h. Mass loss during sulfonation-desulfonation and carbonization will cause the rate to decrease to about 4 kg/h of CF at the CFTF. Precursor fiber for this project will be produced by Dow in Midland using a melt spin line. The melt spin line was configured with a single-screw extruder, a gear pump to control flow rate, a spinning die, a godet roll system for stretching the fibers, and a winder. The configuration of the line is shown in Figure 3. At the start of the project, the melt spin line was rate limited to much lower rates by the configuration of the die and the requirement to stretch the PO precursor fiber to a diameter between 10 and 18 μm . The extruder and gear pump were capable of considerably higher rates and thus they were not rate limiting.

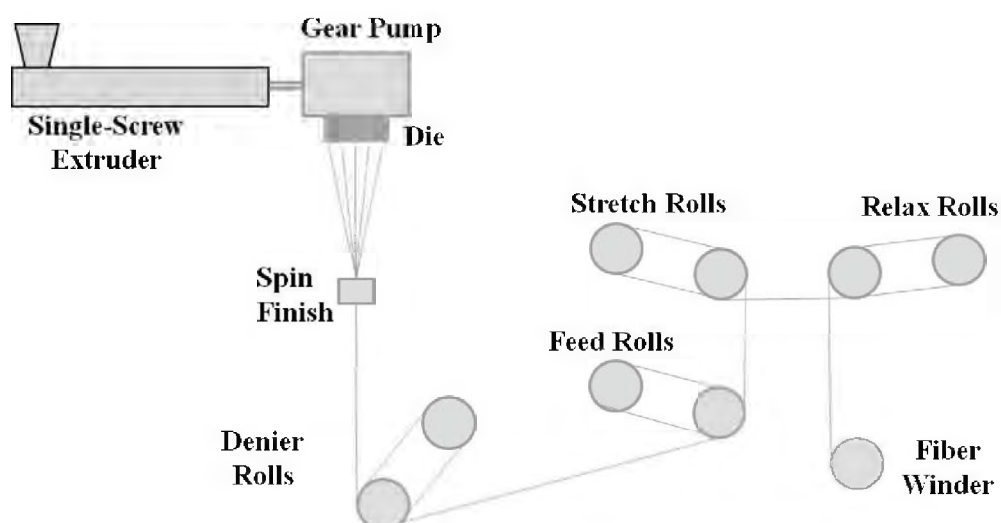


Figure 3. Schematic of the melt spinning line at Dow Midland for producing PO precursor fiber.

Scale up design indicated that the best and lowest cost method to increase the rate of the melt spin line was to replace the current die with two dies, each die with 300 orifices. Several die sets would be made with orifice diameters ranging from 250 to 700 μm . The tows produced here would have 600 filaments with each filament having the proper diameter. About 4.5 kg of fiber would be wound onto a single spool.

Next, 10 spools from the melt spin line would be combined into a single 6k tow at Dow Midland. This 6k tow would be wound onto mill rolls that contain about 40 kg of PO precursor fiber. This precursor fiber would be ready for the sulfonation-desulfonation process.

Scale Up of the Sulfonation-Desulfonation Process

The Dow proprietary sulfonation-desulfonation process is the key operation for this method of producing CF from PO precursor fibers. Since the process is Dow proprietary, many details including process flows, operating conditions, and residence times cannot be discussed here. Instead an overview of the scale up components will be presented.

The 6k tow PO precursor fiber mill rolls will be unrolled at the start of the sulfonation-desulfonation plant using a creel stand, as shown by the schematic (left side) of Figure 4. Tows from four mill rolls will be combined at the start of the process to produce a PO precursor tow with 24k filaments. Numerous 24k tows will be processed in parallel to obtain an overall rate of 5 kg/h at the start of the process. The tows are moved forward at a precisely controlled speed and tension using a series of godet rolls. In between the godet rolls are three sulfonation reactors where the fibers are contacted with the sulfonation solution. The temperature, concentration, and residence times in each reactor are monitored and controlled. After sulfonation is complete, the fibers are washed in water to remove the sulfonation solution. The next set of heated rolls is used to desulfonate the fibers. A spin finish is applied and then the 24k tows are wound onto mill rolls. These mill rolls will contain about 40 kg of desulfonated fiber. They will be shipped to ORNL where they will be carbonized to CF using the CFTF.

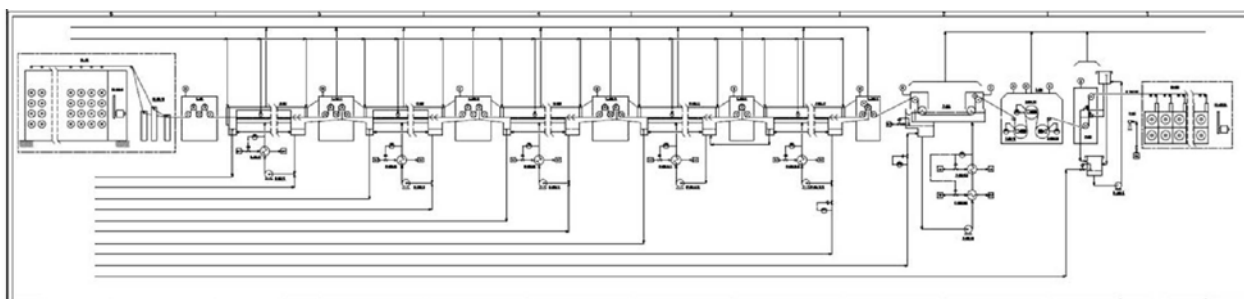


Figure 4. Schematic of the sulfonation-desulfonation market development plant. Mill rolls of PO precursor fiber are unrolled on the left side of the schematic, and the desulfonated fiber is rolled up on mill rolls at the right side.

The sulfonation-desulfonation line shown by the schematic of Figure 4 will be about 100 m in length. A schematic showing the market development sulfonation-desulfonation plant is shown in Figure 5. Other capital items that are necessary to operate the market development line include sulfonation solution and blending tanks, waste sulfonation solution tanks, air scrubbers, loading and unloading stations, utilities, mechanical refrigeration units (MRU), air conditioning and heating units (AHU), a control building, and a testing lab.

The detailed proprietary design of the plant along with all process flow streams was designed. Moreover, the cost estimate for the construction and operation were obtained. This cost estimate was used as part of the Go-No-Go decision that Dow made during June, 2013. Although the cost of the market development plant was higher than originally estimated, it was not the main driver for the Go-No-Go decision by the Dow team. The construction of the plant would only start if the decision to proceed was given and that capital authorization was obtained.

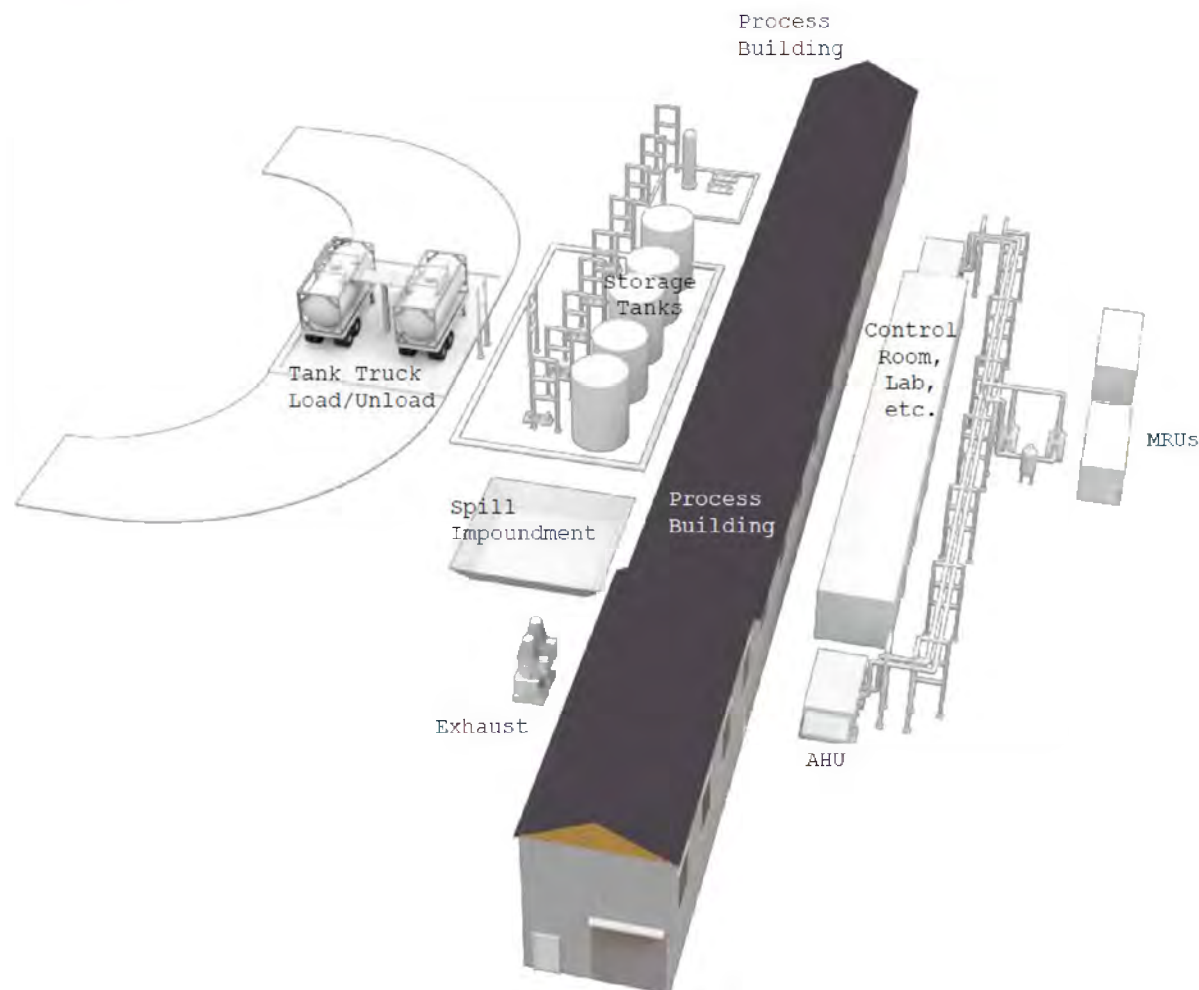


Figure 5. Aerial schematic of the market development line for the sulfonation-desulfonation of PO precursor fiber.

Potential Energy, Economic, Environmental, and Market Benefits for US Manufacturing Industries

PO-based CF has a very large potential long-term impact on energy usage in the automotive sector, due to fuel savings from lighter automobiles. Current PAN-based CFs are too expensive for widespread use in domestic automobiles. The raw materials cost and production technology for PAN-based CF are unlikely to ever achieve a cost low enough to realize widespread use in automobiles. Hence we assert that PO-based CF, because of their lower cost, enable the widespread application of CF and the attendant weight reduction (fuel savings) in the US automotive sector.

The commercialization of PO-based CF offers very large energy and environmental impacts in the US, estimated to exceed 500 Tbtu of energy savings and 60 million metric tons of CO₂ emissions avoidance (about 0.5% of total 2010 US energy demand and 1.0% of emissions) annually by 2036. The primary energy impact is from improved automobile (includes light trucks) fuel economy. Emissions avoidance is about equally shared between renewable wind

energy generation and reduced automotive tailpipe emissions. The automotive benefits tend to accrue slowly, and then accelerate as the rates of market penetration and inventory replacement increase. Upon total automotive market penetration and inventory replacement the impact is potentially 2 Mbpd of oil (4,000 TBtu) in energy savings and 250 million metric tons of CO₂ emissions avoidance annually.

The commercialization of PO-based CFs also creates enormous US employment, primarily driven by the manufacture of CF and composite parts for automobiles, and therefore tracking the automotive market penetration in timing. The economic impact is estimated to be over 100,000 direct manufacturing jobs and 20,000 associated “white collar” jobs within two decades of project completion. Initially slow market penetration and inventory replacement rates are major factors that delay the realization of large energy savings. As shown in Figure 6, it takes roughly a decade after market introduction to achieve 100 TBtu of annual energy savings from improved automotive fuel economy, but after two decades the savings approach 800 TBtu annually. PO-based CF approximately doubles the energy productivity of PAN-based CF production, but as shown in Figure 6 it still is significantly more energy intensive than the production of steel used in automobiles. The very large net energy benefit of about 500 TBtu annually (within two decades after market introduction) shown in Figure 6 is realized in the CF application rather than its manufacture. Upon total market penetration and inventory replacement the impact is potentially up to 2 Mbpd of oil or 4,000 TBtu annually. The market penetration assumptions are discussed below.

Energy Savings

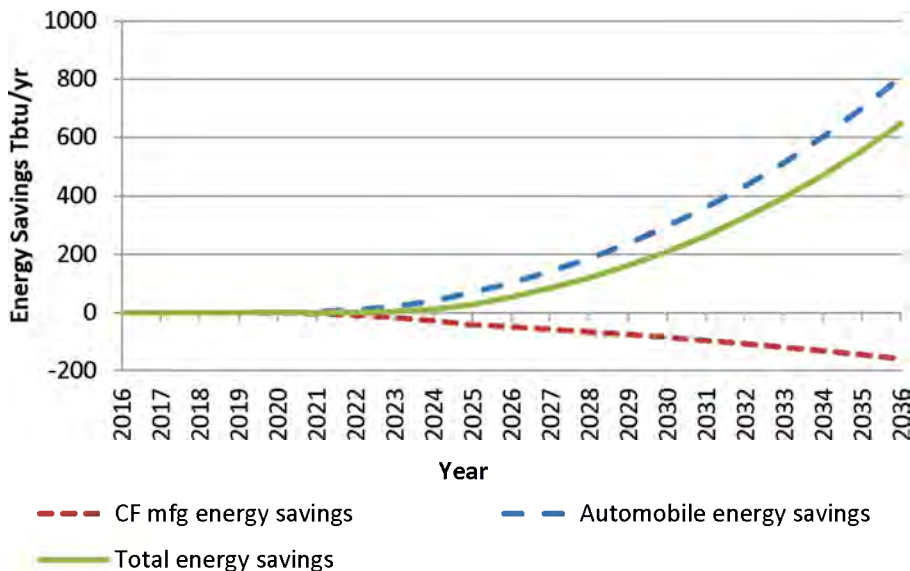


Figure 6. Time profile of US energy savings attributable to PO-based CF.

The net CO₂ emission avoidance attributable to PO-based CF is estimated to exceed 60 million tonnes annually (about 1% of total US emissions in 2010) by 2036. As with energy, the major impact on greenhouse gas emissions is realized in the application of PO-based CF rather than their manufacture, and the effect begins to accelerate about a decade after market introduction due to the time required for automotive market penetration and inventory replacement. Both the

automotive sector and wind energy sector are major contributors to reductions in CO₂ emissions. The automotive sector reduction flows directly from the improved fuel economy; i.e., the tailpipe emissions are proportional to the amount of fuel used. We further estimate that PO-based CF, because they reduce capital cost for multi-megawatt wind turbines, will result in increased wind energy power generating capacity that emits no CO₂. Both the automotive and wind energy contributions to CO₂ emissions avoidance are shown in Figure 7. The wind energy impact shown in Figure 7 is limited to that from the increased wind energy market share attributable to the lower cost of PO-based CF; i.e., wind energy capacity that would not have been realized if only PAN-based CF were available.

CO₂ Emission Avoidance

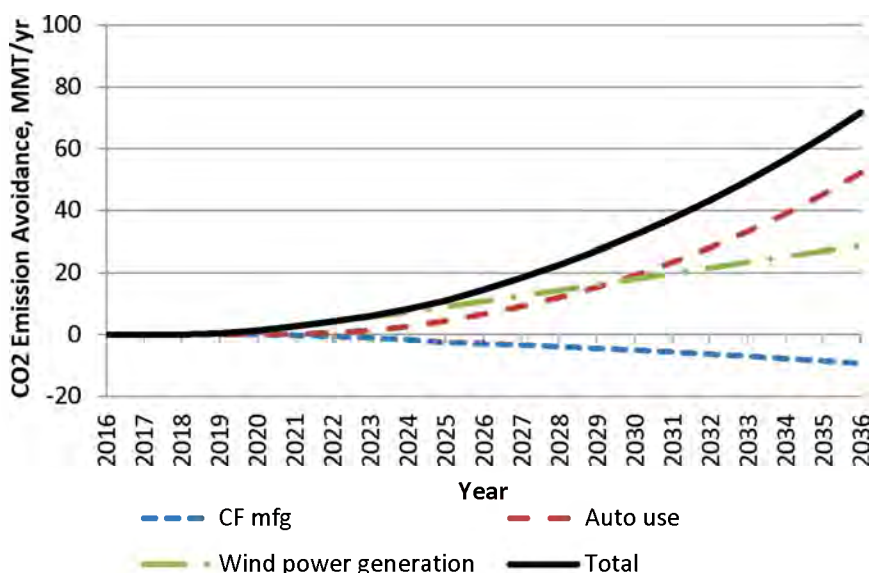


Figure 7. Time profile of US CO₂ emissions avoidance attributable to PO-based CF.

As is the case for the energy savings discussion above, the manufacture of CF results in greater net emissions than if steel were used for automobile manufacture, but the reduction in emissions during the automotive life cycle is a much larger effect. CF manufacture from PO precursors produces lower emissions than the manufacture from PAN precursors. The projected automotive demand for CF, however, is so much larger than that for wind energy that the automotive sector dominates with a resultant increase of CO₂ emissions from fiber manufacture versus manufacturing the competing materials. Upon total automotive market penetration and inventory replacement the impact is potentially up to 250 million tonnes CO₂ avoidance annually. The market penetration assumptions are discussed below.

The cash cost to manufacture PO-based CF is estimated to be about 20% less than that of today's PAN-based CF technology. The cost advantage is primarily attributable to i) lower raw material cost for PO versus PAN, ii) a significant cost advantage of melt spinning for PO precursor fiber production versus solution spinning required for PAN precursor fiber production, and iii) higher chemical yield in conversion to carbon fibers; i.e., greater than 70% for polyethylene versus about 50% for PAN.

The CF fiber market has historically been dominated by aerospace and defense applications, but

industrial applications have recently surpassed them in terms of product volume. Based on current PAN technology, industrial markets are projected to account for 75% of volume (60% of value) of a 150k tonnes/yr (\$3 - \$5 billion) market for CF alone in 2020. In 2010, the global CF market totaled approximately 40k tonnes, with 60% (24k tonnes) directed to industrial markets at an average price of \$10 - \$14/lb. A 50% cost reduction would correspond to economic savings of up to \$375 million/yr in 2010 and up to \$1.2 billion/yr in 2020. However, the truly game-changing impact is explosive market growth spurred by the lower material cost of PO-based CF. We estimate that the introduction of low-cost PO-based CF will spur explosive growth such that by 2036 the US automotive market alone will consume roughly 1M tonnes/yr of carbon fiber (more than 10X today's total global CF demand). That market will not materialize with the current PAN technology and foreseeable PAN fiber pricing. The basis of these projections is discussed below.

Successful demonstration of the technology will allow a decision to commercialize the technology in 4 years. PO-based CF commercialization could occur in 5 to 7 years. Figure 8 shows an estimated impact approaching 130,000 jobs by 2036. This includes about 45,000 CF manufacturing jobs, 65,000 downstream manufacturing jobs, and about 20,000 engineering, sales, and manufacturing jobs. This is based on Kline and Company's estimate that about 50 total workers are needed at the fiber spinning and heat treatment factories to manufacture 1,000 tonnes of carbon fiber [11] and the market penetration estimates discussed below.

Job Creation

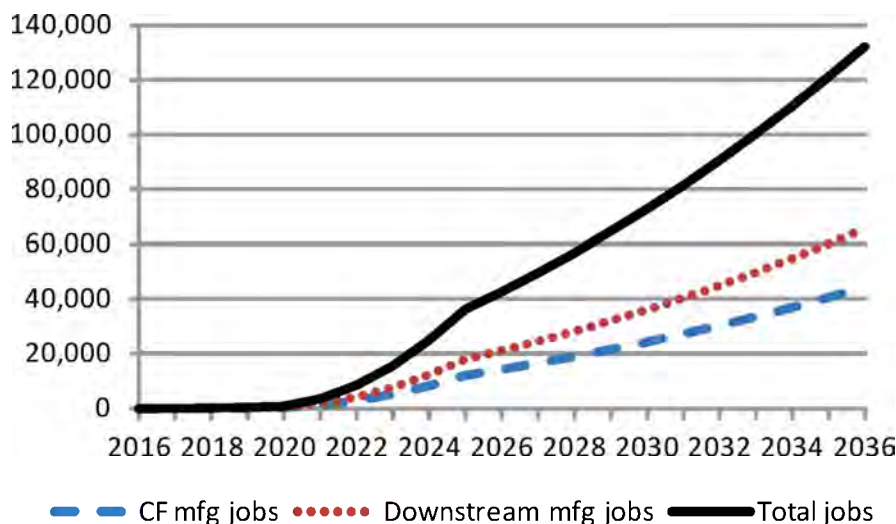


Figure 8. Estimated jobs impact of PO-based CF manufacturing.

We expect that polyolefin-based CFs will ultimately have major, broad impact on the CF market across many applications. However, we are focusing this proposal and the initial market entry on the automotive and wind energy markets, both of which are potentially huge markets with major impact on US energy and environmental security.

We expect that, lacking disruptive market drivers such as rapid doubling of fuel prices, PAN-



based carbon fibers will always be too expensive for widespread use in high-volume, mainstream automobiles sold in the US market. We assert that widespread application of carbon fiber composites in the US automotive market, with its attendant fuel efficiency benefits for the nation, is likely to occur only if significantly lower-cost CFs are introduced into the market. We expect PO-based CF to be the disruptive technology that enables widespread CF composites adoption in the mainstream US automotive market.

For purposes of the current market analysis, we assume that PO-based CF technology begins to be adopted by the market in 2017. We expect the automotive adoption rate to be relatively slow in the early years, as the industry becomes familiar with the technology. We assume that after four years, only 5% of the new automobiles sold in the US will contain CF composites, and the average content among those 5% of automobiles will be 10 lb of carbon fiber. After this cautious introductory period, the pace of adoption will accelerate dramatically, driven by record low CF prices and new confidence in their durability, combined with likely regulatory pressure to improve fuel economy. We project that by 2025, 40% of new automobiles sold into the US market will contain an average of 100 lb of CF per vehicle. After this frenetic growth period, the growth rate will relax somewhat, achieving 75% market penetration by 2036, with average content in those vehicles being approximately 200 lb of CF.

The US automotive market has experienced significant contraction in recent years with 11.5M units sold in 2010. For all estimates in this proposal we have conservatively assumed that the market continues at this annual sales volume through 2036. Heavy trucks also are a potential market with early entry opportunities but small compared to light automotive and thus not included in these projections.

Our second focal market, wind energy, does use PAN-based CFs at current prices, but the lack of stable CF supply and pricing is a significant inhibitor of CF use in that market. The compression strength of CF composites is an additional concern for their use in wind turbine blades, but these issues typically arise from poor process control in the composite manufacture and can be readily addressed by automation and improved quality control. PO-based fibers potentially offer some advantages for manufacture with specific functionality to address composite compression strength that can be imparted in the melt spinning process.

The US wind energy market experienced rapid growth in the early 2000's, growing to 10 GW of new capacity installed in 2009. The US market is now fluctuating, with annual new capacity installations forecast to range from 4.5 to 8.0 GW through 2016 [12]. Based on that forecast, we assume a baseline market of 6 GW of new capacity installation in 2016, with steady growth back to 10 GW of new capacity annually by 2025 and flattening at 10 GW annually thereafter. We expect that PO-based CFs, because they are less expensive than PAN, will enable a lower cost of wind-generated electricity, making wind energy more competitive with fossil-fueled power generation, and will thus create an additional 10% of new capacity annually that would not otherwise exist. Based on this growth scenario, we estimate the installation of about 200 GW of new "baseline" wind generation capacity from 2016 to 2036, plus an additional 16 GW of new capacity that occurs solely due to the availability of lower-priced PO-based CFs. The baseline capacity would be added regardless of the availability of PO-based CFs, but we assume that because of its lower cost, PO-based CFs will make steady gains to achieve 75% market



penetration by 2030 and thereafter. We are not aware of any rigorously developed market forecasts that cover the time period from 2016 to 2036; these assumptions are much less aggressive than the growth rates required to achieve DOE's goal of 20% of US electricity generated by wind in 2030 [12].

The estimate of energy used in the production of PAN-based CF is derived from an independent cost assessment of PAN-based CF by Kline and Company [11]. The estimate of energy used in manufacturing PO-based CF is from an internal ORNL extension of that analysis to PO. The estimate used for steel is from an ORNL publication comparing the life cycle effects of a steel automotive part versus the same part made from various CF options and composites fabrication processes [13]. The estimates of CO₂ emissions associated with the production of CF or steel are based on the energy used in their manufacture, and the emissions per unit of electricity generated or natural gas used [14].

The automotive fuel savings are estimated from the general rule that 10% vehicle weight reduction delivers about 7% reduction in fuel demand [15]. The limits of CF composites use in automobile design and manufacturing are taken from Boeman and Johnson [16]. Automobile weight reductions were estimated from the Auto/Steel Partnership's mass compounding calculator [17]. Total US vehicle inventory (235M), 2010 new vehicle sales, and petroleum demand data are from the Transportation Energy Data Book [18]. The inventory replacement period of 20 years is also calculated from these data. The automotive market penetration rate is based on the standard method of introducing new technology into the automotive platform, with consideration of expected market drivers such as fuel prices and impending regulation. The market penetration rates were developed in discussions among Dow, Ford and ORNL.

The US wind energy market outlook data are from a presentation at the GoCarbon Fiber 2011 conference [19]. Wind energy capacity factor used to estimate net wind power generation from rated capacity was from DOE's "20% Wind Energy in 2030" report [12]. The projected increase in the wind market is based on the assumption that a small decrease in the cost of energy, due to lower materials cost, will render wind energy more favorable than other options and result in a small increase in the market growth rate.

Estimates of jobs created in CF manufacturing are based on data from Kline and Company [11]. We estimate there will be 1.5 downstream jobs manufacturing automotive or turbine blade parts for every CF manufacturing job. We also estimate that one white collar job will be generated for every five manufacturing jobs.

Levelized Economic Cost of the Process

During budget period 1, the Dow sponsored discovery team continued to refine the mass balances, energy balances, and cost analysis for the sulfonation-desulfonation route to CF from PO precursor fiber. Here, the economic analysis of the CF production process from PO precursor fibers was evaluated relative to the conventional PAN process technology. Numerous analyses were performed studying the cash cost, manufacturing cost, and the levelized economic cost of the processes. The cash cost is the sum of raw materials and packaging costs, utilities, labor, maintenance, and overhead costs. The manufacturing cost is the sum of the cash cost and the



depreciation cost of the total investment. The levelized economic cost is the sum of the cash cost and the levelized capital cost (depreciation cost and the return on investment). The cash cost to manufacture CF from PO precursors is advantaged over fibers produced from PAN precursor fiber. This result is driven mainly by the lower cost of PO resin, the ease of melt spinning PO resin to fibers, and the higher yield of PO to CF as compared to the PAN based process. The capital required to sulfonate the fibers adds a significant cost to the process due to the need for investment in a sulfuric acid recovery plant. This high additional capital over the capital for a PAN based CF plant, reduces the levelized economic cost to slightly advantaged over PAN based CF. The sulfonation-desulfonation stabilization route failed to meet the Dow's return on investment criterion and the cost advantage target set forth for the DOE project.

The existing market for CF of all types is currently quite weak with available supply higher than demand. The oversupply was created by new carbon suppliers entering the market, increased efficiencies of suppliers' carbon fiber production lines, and contraction in some markets [20]. This oversupply condition has reduced the selling price for many carbon fiber grades. For example, it is rumored that the selling price of Toray T300 CF is currently in the \$15/kg range. Selling at this price is likely to recover the cash cost of producing CF while not paying for the depreciation of the equipment and the interest on the capital cost.

Based on the levelized cost for the PO precursor route to CF using the Dow proprietary sulfonation-desulfonation process providing only a slight incremental reduction over the PAN based process, Dow has elected to abandon the process. The risk was too high for the capital investment for this level of incremental reduction in levelized economic cost.

In June, 2013, Dow made the No-Go decision to halt and abandon the Dow proprietary sulfonation-desulfonation process for stabilizing PO precursor fibers for the manufacturing of CF. This No-Go decision was identified in the original proposal and at the start of this project, and the decision was made as scheduled. The decision was based on the high levelized economic cost of the process relative to the manufacture of CF from polyacrylonitrile (PAN) precursor fibers.

Benefits Assessment

The benefits of producing CF from PO precursor fiber were clearly identified in the Results section. These benefits still exist even though the Dow proprietary sulfonation-desulfonation process did not meet the economic constraints for Dow investment. Other routes for the stabilization of PO precursor fiber may allow a low cost route to CF without the high cost burden of the need for a sulfuric acid recovery plant.

Commercialization

Due to the high levelized economic cost, Dow decided not to commercialize the sulfonation-desulfonation route for manufacturing CF from PO precursor fiber.



Accomplishments

During the first budget period, the project funded under DOE award number DE-EE0005760 was on schedule with preparation and planning for the development of a market development scale process capable of producing CF at a rate of 4 kg/h in the third budget period. The CF would target properties that met or exceeded the Department of Energy Vehicles Technology [1] standard; i.e., 172 GPa modulus and 1.72 GPa strength at greater than or equal to 1% strain. The Dow proprietary process was capable of meeting and exceeding these targets properties. Accomplishments in the first year included the following:

- Design of the entire process that included melt spinning of PO precursor fiber (at Dow), combining of the precursor fiber to 6k tows (at Dow), stabilization of the fibers using the Dow proprietary sulfonation-desulfonation process (at Dow), carbonization of the desulfonated fiber to CF (at ORNL using the CFTF), surface treatment and sizing of the fiber (at ORNL using the CFTF), and property and composite testing by Dow and Ford.
- Redesigned the melt spin line at Dow to produce tows with 600 filaments (a 0.6k tow) at a rate of 5 kg/h. The filaments would be 10 to 18 μm in diameter. A combination station was designed that would take 10 spools of 0.6k tow PO precursor fiber and produce a 6k tow.
- Designed a market development sulfonation-desulfonation plant that would take the 6k tows of PO precursor fiber and produce 24k tows of desulfonated stabilized tows that would be ready for carbonization at ORNL's CFTF. Mass and energy balances and the cost to build the plant using the Dow proprietary sulfonation-desulfonation process were detailed.

Products

No products were produced during this project.

Publications, Conference Papers, and Presentations

No publications, conference papers, and presentations were produced from this project.

Inventions, Patent Applications, and/or Licenses

No inventions, patent applications, and/or licenses were produced from this project.

Graduate Students Thesis Based on the Project Work

No research was performed by Graduate students for this project.

Websites or Other Internet Sites

No Websites were produced for this project.



Conclusions

The project started in September, 2012 with the goal of the scale up from existing laboratory scale process for producing carbon fiber (CF) from polyolefin (PO) based precursor fiber using a Dow proprietary sulfonation-desulfonation stabilization process. The award was used to develop a process that was capable of producing market development quantities of CF from PO precursor fiber at a rate of 4 kg/h of CF. The CF would target properties that met or exceeded the Department of Energy (DOE) Vehicles Technology [1] standard; i.e., 172 GPa modulus and 1.72 GPa strength at greater than or equal to 1% strain. The Dow proprietary process was capable of meeting and exceeding these targets properties. Project DE-EE0005760 resulted from a Collaborative Research and Development Agreement (CRADA) between Dow and Oak Ridge National Laboratory (ORNL) with support from the Michigan Economic Development Corporation (MEDC) and DOE.

In the first budget period, the main goal was to design a sulfonation-desulfonation market development plant capable of stabilizing PO precursor fiber at a rate of 5 kg/h using a sulfonation solution. The detailed design, location, and cost estimate were determined as scheduled in the Project Management Plan (PMP). In parallel with this DOE award project was a fundamentals and economic evaluation funded by The Dow Chemical Company (Dow). The goal of the Dow sponsored project was to finalize the mass balances, energy balances, and levelized cost to produce CF using the Dow process. A Go-No-Go decision was scheduled June, 2013 based on the findings of the DOE sponsored scale up project and the Dow sponsored project.

In June, 2013, Dow made the No-Go decision to halt and abandon the Dow proprietary sulfonation-desulfonation process for stabilizing PO precursor fibers for the manufacturing of CF. This No-Go decision was identified in the original proposal and at the start of this project, and the decision was made as scheduled. The decision was based on the high levelized economic cost of the process relative to the manufacture of CF from polyacrylonitrile (PAN) precursor fibers.

The DOE and Dow decided to halt spending on the project until a new PO fiber stabilization process could be identified that met the DOE physical properties standard and the levelized economic cost constraints of Dow. When the new technology was developed, then award DE-EE0005760 would be re-started with the same goals of the development of a market development plant capable of producing CF at 4 kg/h with the properties that met or exceed those set forth by the Department of Energy Vehicles Technology. Progress on the development of the new process has been slow and thus has delayed the scale up project.

Dow's efforts to date have not progressed to the point of demonstrating a commercially-viable process for production of low cost CF from PO precursors for Dow's rigorous economic constraints. After extensive discussions within Dow and consultation with DOE's Advanced Manufacturing Office (AMO) Headquarters and Golden Field Office teams, Dow has decided to proceed with the formal recommendation to terminate subject project. DOE's AMO Headquarters and Golden Field Office teams agreed with the termination of the project.

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