02FCC-144

High-Volume, Low-Cost Precursors for Carbon Fiber Production

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ABSTRACT

Carbon fiber composite use in automobiles and light trucks could dramatically reduce energy use and engine-out emissions. However, worldwide capacity of 28,000 tonnes per year of carbon fiber from polyacrylonitrile (PAN) and petroleum pitch could support limited automotive use. Production of high-volume, industrial-grade fiber from renewable and recycled polymers (lignin, recycled plastics, regenerated cellulosics) could meet automotive demand. Profiles of material volumes, carbon content, and melting points indicate several attractive candidates for production melt-spun carbon fiber feedstocks. Effects on the carbon fiber production cycle and its integration into automotive production are discussed.

INTRODUCTION

The transportation industry will likely be faced with increasingly tight controls on engine-out emissions and, possibly, on corporate average fuel economy, or CAFE. These standards could be met in the U.S., as in Europe, with the production of smaller, more fuel efficient vehicles. Historically, the domestic consumer prefers larger, higher performance vehicles. Lowering the weight of automobiles and light trucks, through the use of carbon fiber composites, could decrease emissions and increase fuel economy without decreasing size or performance.

Conceptually, the use of carbon fiber composites in transportation applications would seem straightforward. Carbon fiber composite use in aerospace (airplanes and missiles) and consumer (golf club shafts and fishing rods) applications has been successful. Racing cars, too, employ carbon fiber composites for high performance and lightweight.

All of these applications stress high performance rather than cost, availability, and rapid manufacturability.

The automotive industry is both very high volume and highly cost competitive. For a successful application, carbon fiber and composites production must be optimized for lower cost and higher availability. Additionally, production of the high volumes of fiber needed will place new environmental constraints on production of carbon fiber feedstocks: the automobile industry has a commitment of environmentally-sound production of materials and to recycle and reuse of industrial materials.

To meet goals of the automotive industry for environmentally friendly production of low-cost carbon fiber, high volumes of environmentally friendly feedstocks and novel production technologies will be required. This paper presents the results of surveys profiling availability, cost, and likely carbon fiber yield from a variety of renewable and recycled fiber precursors and compares material availability to current needs for automotive materials.

MATERIALS USE IN AUTOMOBILES AND LIGHT TRUCKS

Decreasing the overall weight of passenger vehicles could significantly increase fuel efficiency and decrease emissions. There are two ways to cut vehicle weight 1) decrease the size of the vehicle and 2) increase the strength and stiffness of the materials used the vehicle so that less material is required.

Although the use of lightweight materials in light transportation is increasing, nearly 1-1/2 tonnes of materials are needed to produce the average automobile. More than half of the materials in an automobile are, as shown in Figure 1, iron and steels. From 1978 to 1997, the fraction and amount of ferrous metals has decreased from 80% to 62% and the fraction of light materials, such as plastics and aluminum, has increased. Part of this is due to the replacement of iron and conventional steel by high strength steels and aluminum. However, the average automobile weight decreased by roughly 100 kg between 1978 and 1997. This is less than 5% of total vehicle weight.

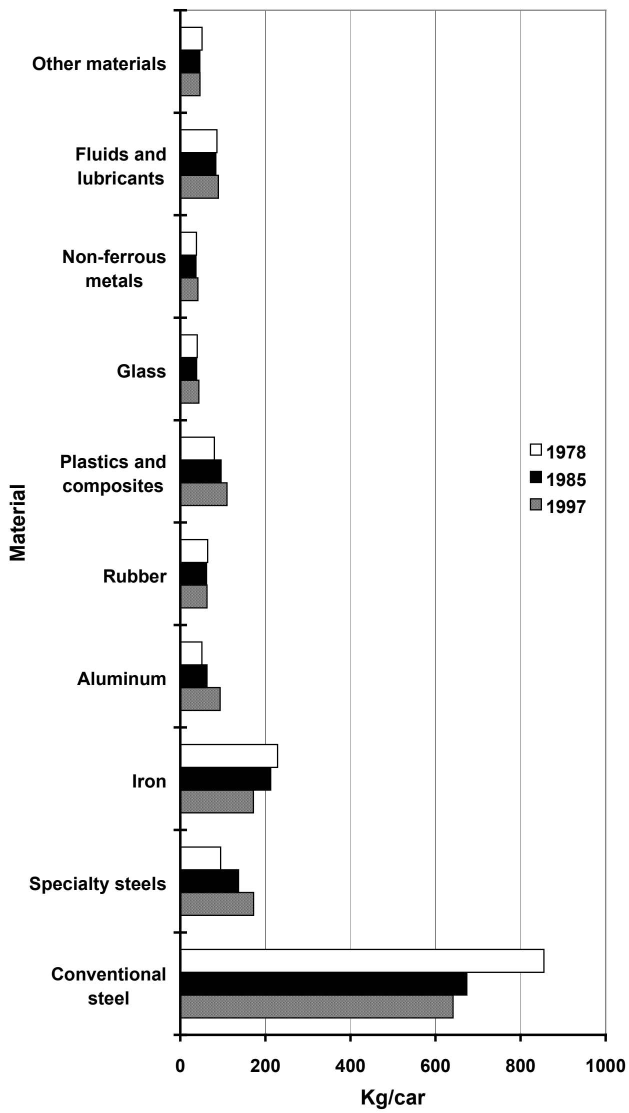

Figure 1. Materials used in an automobile. Adapted from data developed by Ward's Automotive Yearbook. (1)

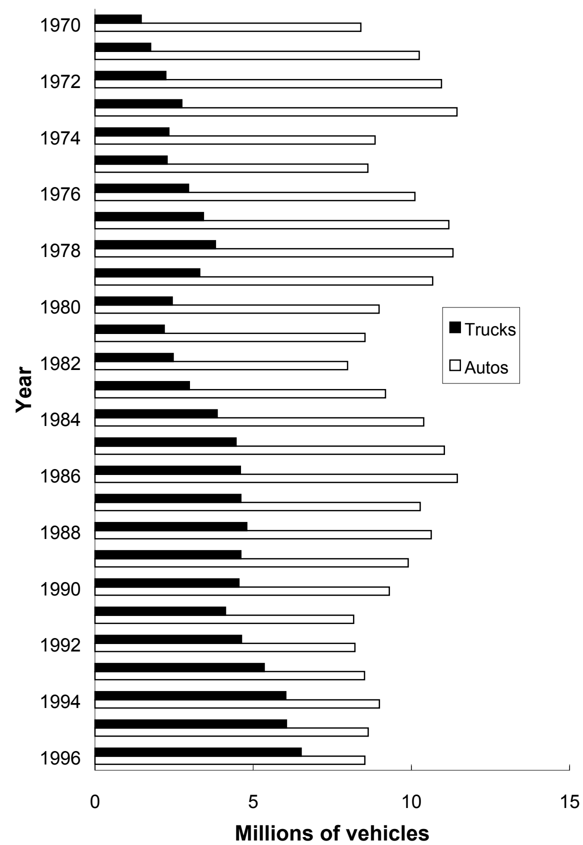

Figure 2. Production of automobiles and light trucks vehicles between 1970 and 1996. Adapted from American Automobile Manufacturers Association, 1997 (2).

As shown in Figure 2, the automotive industry annually produces 15 million cars and light trucks. To replace the 985 kg of ferrous metals in an average vehicle with one-half the weight of 60% carbon fiber resin would require nearly 300 kg of carbon fiber. Production of 15 million light vehicles would require roughly 4 million tonnes of carbon fiber to replace all of their ferrous metals.

The current production capacity for carbon fiber is estimated at 28,000 tonnes per year, or less than 1% of the weight needed to completely replace ferrous metals in passenger vehicles. Additionally, the cost of the carbon fiber-resin composite would need to be roughly comparable to that of the ferrous materials replaced.

Production of the materials needed for carbon fiber composites, together with development of technologies, which permit their effective use in the rapid throughput manufacturing systems needed for automotive manufacture, poses a significant engineering challenge. It also presents a wide-ranging opportunity to decrease emissions, decrease U. S. domestic fuel consumption, and directly sequester carbon so as to meet Kyoto or European Union carbon sequestration requirements or product credits.

PRODUCTION OF CONVENTIONAL CARBON FIBER FEEDSTOCKS

The major carbon fiber feedstocks are polyacrylonitrile (PAN) and pitch. Both of these materials are primarily petroleum derived. PAN fiber is prepared using a multistep process such as the one shown in Figure 3. The process is tailored to production of a high quality, highly clean fiber, which has a low content of solid contaminants. Pitch fiber is directly spun from a melt.

Once feedstock fiber is prepared, carbon fiber is prepared in a series of steps shown in Figure 4. Essentially, the process for PAN fiber starts with hot-stretching. Processing for both pitch and PAN fiber then involves thermosetting in an air or oxygen atmosphere. The fiber is then carbonized and graphitized in a reducing atmosphere. Graphitized fiber is surface treated, sized, and spooled for use. The process is typically performed using long lengths of multiple fiber (tow), which pass through series of furnaces.

Thus, producing carbon fiber requires two separate facilities - a feedstock production facility and a carbon fiber production facility. The feedstock, power requirements, and emissions vary with the type of fiber being

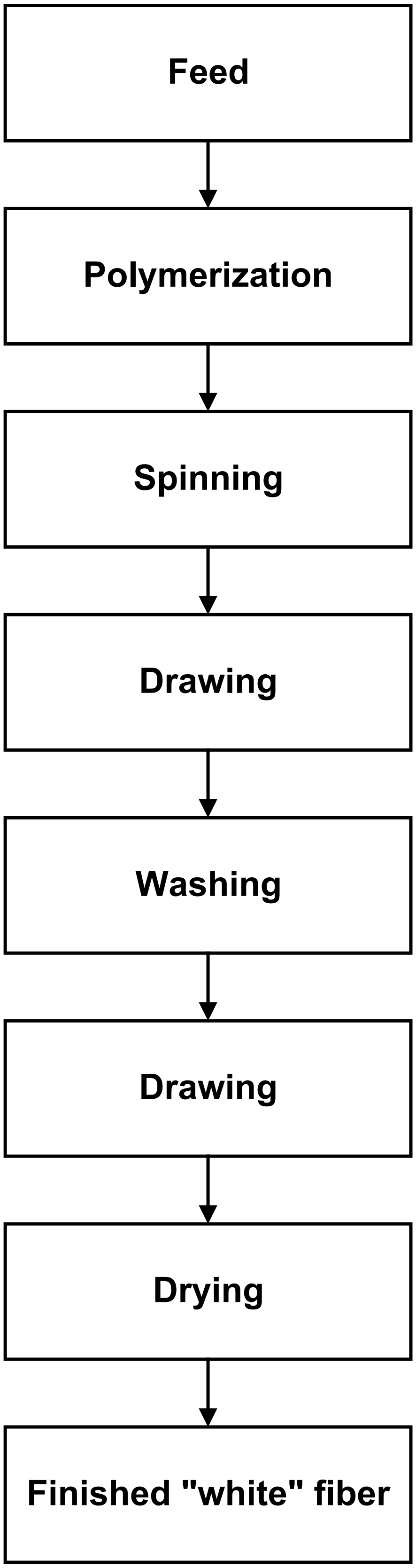

Figure 3. Preparation of PAN fiber feedstock for carbon fiber production.

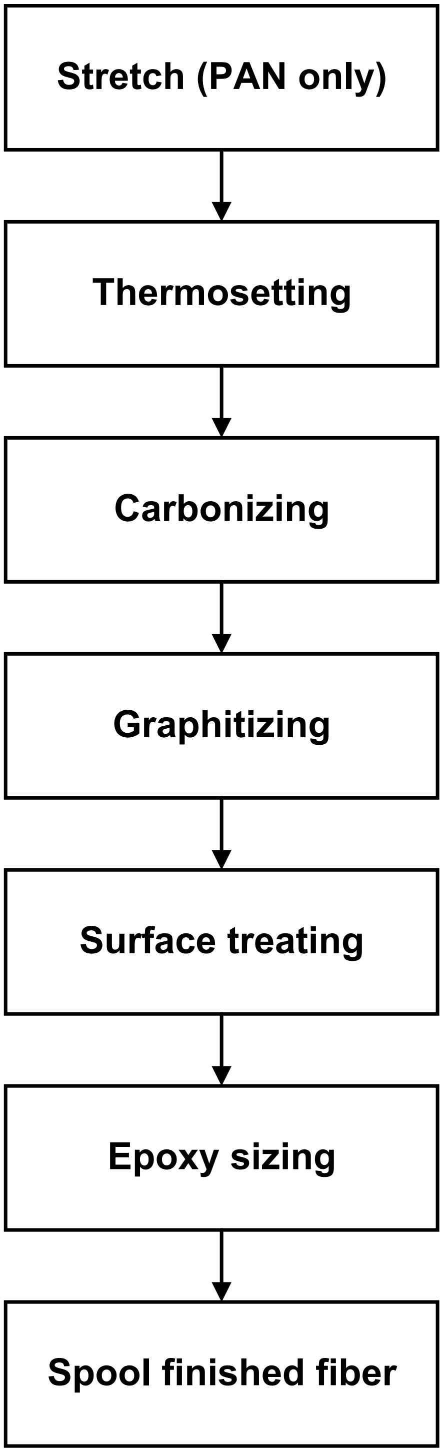

Figure 4. Production of carbon fiber from pitch or PAN feedstock.

produced. A graphitization facility requires both good emissions control and significant amounts of power to provide process heat in graphitization. Low yields (weight carbon fiber/weight feedstock) from rayon and other low-carbon fibers, can further increase overall demands for capital and energy.

As the current price indicates, there are significant opportunities for reduction of cost and energy in carbon fiber processing. For example: 1) high-yield feedstocks which minimize the size of carbon fiber production facilities; 2) high-volume renewable or routinely recycled feedstocks which reduce raw fiber production and facilities costs; 3) low-cost, environmentally friendly techniques; such melt-spinning raw fiber, to minimize production costs, and emissions; 4) fibers which produce low or minimum toxicity furnacing emissions; 5) integration of furnacing into production facilities with waste heat or low-valued electricity; and 6) novel rapid or low energy production techniques could be developed. Considered together, these approaches could increase capacity and decrease cost sufficiently to encourage widespread use of low-cost carbon fibers in passenger transport.

HIGH-VOLUME CARBON FIBER AND RESIN FEEDSTOCKS FROM RENEWABLE OR RECYCLED MATERIALS

Feedstock price is a major component of carbon fiber production cost. At present, the cost of producing white polyacrylonitrile fiber, the predominant feedstock for industrial carbon fiber, is estimated at ~$1.55/kg and the yield from this material is around 50% w/w. Production of industrial grade carbon fibers from renewables or recycled polymers is attractive in that it provides an inexpensive, high-volume stream of feedstock at a reasonable price. Historically, a wide variety of different polymers have been used as carbon fiber feedstocks. These include blends of polymers with pitch and other aromatics, such as polystyrene and pitch blends (3) or polymerizable napthalene derivatives (4); conventional fibers, such as nylon (5) or coated Kevlar (6); cellulosics, primarily rayon (7,8); and lignin blends (9), thiolignins (10), or lignosulfonates (11). Several feedstocks produced carbon fiber which was roughly comparable in properties with the pitch and PAN fibers of the period. Inorganic contaminants, especially those which aggregated to form particulates, were a particular problem as such defects were often found at fiber breakage sites.

Isotropic pitch, a byproduct of petroleum and coke production, can be melt-spun to provide a high-yield carbon fiber feedstock. However, the time required for stabilization and oxidation is lengthy (12). General purpose fibers produced from isotropic pitch are light weight, have good electical conductivy and are resistant to chemicals, heat, and abrasion. However, they have low tensile strength and modulus in comparison to high performance graphite fibers used in resin composite applications and are currently produced in limited quantity (13).

At present, several streams appear to be attractive carbon fiber feedstock. Growth of the environmental movement has made significant amounts of polystyrene, polyethylene, polypropylene, and poly (ethylene terephthalate) available at relatively low costs (14). Typical prices for spot-market for recycled polyesters, polyolefins, cellulosics, and textile fibers are shown in Table 1. Long-term or in-house prices are likely to be significantly lower. The current price of the highest-volume domestic lignin compound, calcium lignosulfonate, has remained in the range of $0.04-0.10/kg for decades (15).

Table 1. Prices of recycled and renewable polymers which can be used as carbon fiber feedstocks.

Material	Cost, $/kg	Reference
Preconsumer recycled resins		
Expanded polystyrene	0.07	14
High-density polyethylene	0.01	14
Isotropic pitch	N/A*	13
Low-density polyethylene	0.01	14
Polypropylene	0.40	14
Polystyrene	0.35	14
Postconsumer resins and fibers		
Poly (ethylene terephthalate)	0.26	14
Polyester	0.31	14
Nylon	0.42	14
Rag stock	0.07	14
Renewable materials		
Lignosulfonate, calcium, U. S.	0.05	15

*Regarded as proprietary by current manufacturers.

High quantities, perhaps 90,000 tonnes per day, of Kraft lignin and cellulosic wastes, are currently burned to fuel paper mills (16). These materials are centrally collected and their processing technology is well understood. The amount of available lignocellulosic materials is expected to increase significantly if use of biomass fuels, such as ethanol blends with gasoline or chipped wood power plant fuel, becomes more attractive.

Domestic production of renewable and recycled materials is probably adequate to support production of enough carbon fiber to replace all of the ferrous metals used in passenger transportation. It is also likely, based on earlier research, that carbon fibers could be produced from blends of different recycled materials.

A combination of renewable and recycled materials may also provide feedstock for the production of resins. Recent papers indicate that lignin can be used to supplement resins for use in composites (17) as can the epoxides of vegetable oils (18). It may also be possible to recycle part of the 3.6 million tonnes of automobile shredder fluff produced annually into resin blends (19,20).

The wide variety and high volumes of recycled and renewable materials available in the domestic market appear sufficient to support the production of enough carbon fiber and enough resin to replace all of the ferrous metals used in passenger transport.

YIELDS FROM CARBON FIBER FEEDSTOCKS

Yield, measured as weight carbon fiber per weight of raw feedstock, is a critical factor in evaluating the feasibility and cost of carbon fiber production. If yield is low, production of carbon fiber will require larger amounts of feedstock and will also require much larger facilities. This adds to the cost of producing rayon fiber, a regenerated cellulosic. Low yield also results in increased emissions.

Expected carbon fiber yield can be estimated using a combination of the carbon content of individual materials (upper limit) and the char index (lower limit). Reported yields of carbon fiber from pitch, PAN, and rayon fibers are shown in Table 2. Yields of lignin, as developed in our studies, are approximately 0.5.

Table 2. Carbon yield from various precursors

Precursor	Fraction carbon	Expected yield	Reference
Rayon	0.44	0.10-0.30	15
Pitch	0.92-0.96	0.80-0.90	15
PAN	0.68	0.33-0.50	21
Lignin	0.68	0.45-0.55	
Polyethylene terephthalate	0.58		
Polyethylene	0.85	0.09-0.40*	22
Polypropylene	0.88	0.05-0.54*	22

*Higher yields require complete sulfonation of fiber

It is difficult to carbonize and graphitize pure polyolefins and the yields are low. If the fibers are sulfonated using concentrated acids, however, the yields can be increased to feasible levels.

CARBON FIBER PRODUCTION

Figure 1 showed that a “parallel” production facility was required to produce fibers, such as polyacrylonitrile, from solution. However, the disposal or recycle of the solvent from which the fibers are spun is costly and creates environmental emissions. For example, effluents and emissions from the rayon process have limited its use within the U. S. and thereby limited its use as a carbon fiber feedstock.

The bulk of recycled polymers (polyolefins and polyesters) will be melt spun (or melt extruded) to form fibers. Recent reports (23, 24, 25) indicate the possibility of melt spinning renewable Kraft lignin and lignin blend fibers. Although low melting temperatures could present some problems in the stabilization portions of the processing cycle, melt spinning also presents a significant opportunity for cost reduction and effluent reduction.

Melt-spinning is a unit operation which can be incorporated as the first step of the carbon fiber production line. This has the advantage of lowering fiber production capital and operating costs and permitting use of routinely recycled polymers, such as polyethylene.

NOVEL PRODUCTION TECHNIQUES WHICH COULD REDUCE PROCESS ENERGY AND TIME OR WHICH PROVIDE ACCESS TO LOW COST FUELS.

There are two promising technologies which could provide access to low cost fuels which could decrease the overall production time and energy requirements for carbon fiber. One of these is microwave-assisted plasma processing and the other, pulp mill black liquor gasification.

MICROWAVE-ASSISTED PLASMA PROCESSING

Paulauskas and coworkers have been evaluating rapid techniques for processing large tow using microwave-assisted plasma (26). This rapid technique produces PAN carbon fibers which have properties indistinguishable from conventional. However, this continuous technique has several advantages over conventional processing methods: 1) processing is orders of magnitude faster than conventional furnacing methods, 2) econometric studies indicate that microwave assisted plasma processing will reduce the overall furnacing cost for fiber by ~ 21%, and 3) the technique sharply reduces the production of hazardous gaseous emissions from PAN graphitization.

This technique does not eliminate furnacing during the production of carbon fiber from PAN. Hot stretching and low temperature stabilization/oxidation are presently required prior to plasma processing.

PULP MILL BLACK LIQUOR GASIFICATION

Capital equipment used for the Kraft process, which dominates the domestic pulping industry, is aging. The industry has, for several years, been exploring the use of a combined gasification - turbine electric generation process to replace the boilers which burn lignin and recycle process chemicals. Early tests of various process configurations have been successful and the technology is being evaluated in large pilot studies (27, 28).

A successful implementation of gasification technology within the pulp and paper industry could provide: 1) a fuel gas stream and reduced-cost electric power to supply energy for furnacing; 2) significant amounts of lignin, a likely carbon fiber feedstock, which will be recovered and dried to smooth feed rates and load; and 3) in some configurations, available process heat up to 950°-1000°C. These features have the potential to greatly reduce the overall cost of carbon fiber furnacing and handling operations.

IMPACT OF BOTH PROCESSES

Microwave-assisted plasma processing and black liquor gasification are likely to be synergistic for several reasons: 1) microwave-assisted plasma processing requires stabilized and oxidized fiber feedstock which can be produced using the mid-level gasification heat, 2) microwave-assisted plasma processing costs would be reduced in proportion to reductions in costs for electric power, and 3) carbon fiber could significantly improve the economics of wood pulping.

A SCENARIO FOR PRODUCTION OF CARBON FIBER FEEDSTOCK FROM RENEWABLE AND RECYCLED POLYMERS

Roughly 10% of the 85,000 tonnes per day of the lignin burned to power a Kraft pulp mill is precipitated, purified, and dried. The inorganics from the lignin are returned to the pulp mill's recycle process.

The dried lignin is mixed with 20% of a recycled blending, or alloying, polymer to provide strength. The polymer blend is melt-spun as multiple-fiber tow. The tow is rapidly stabilized (oxidized). After treatment, the tow is rapidly processed in furnaces heated by gas from the Kraft mill's gasifier. (The fiber could also be processed with microwave-assisted plasma powered by black liquor fired electric generation.) The finished fiber is cleaned, sized, spooled, and sold to the transportation industry.

At the automobile production facility, the carbon fiber is chopped and mixed with ACRES (affordable composites from renewable sources) soybean oil epoxy resin and formed into heavy structural members for automobiles.

In addition to gaining a secure, non-petroleum domestic source of fiber and resin, the automobile company and the paper mill have created several new environmental improvements: 1) soybean oil based resin is both renewable and very slowly biodegradable; 2) by storing biomass carbon directly in a long-term stable form, the pulp mill and the automobile sequester more than a million tonnes per year of carbon; 3) lighter weight automobiles will consume less fuel and have lower overall engine-out emissions.

FEASIBILITY OF PRODUCTION OF INDUSTRIAL CARBON FIBER FROM HIGH-VOLUME RENEWABLE AND RECYCLED SOURCES

The feasibility of melt-spinning carbon fiber feedstock from renewable or recycled materials has been under evaluation at Oak Ridge National Laboratory for two years. The feasibility of producing carbon fiber from renewable and recycled materials has been demonstrated in proof-of-concept single fiber studies. (24,25).

At a single-fiber test level, the study group has demonstrated the feasibility of melt-spinning Kraft lignin blend fibers which incorporate other routinely recycled polymers. These fibers can be processed using conventional hot-stretching and furnacing technologies. Fibers furnaced to 1600° to 2400°C have a high graphitic content, as shown by powder x-ray diffraction and are dense, compact, and smooth-surfaced.

Studies to scale up to multiple fiber spinning are in process.

DISCUSSION

Development of a cost-effective method for production of carbon fibers will require: 1) high-volume, high-yield feedstocks; 2) low-cost fiber production techniques; 3) demonstration of the ability to integrate processing technology into the industrial processes of either polymer producers or recyclers; 4) significant improvements in carbon fiber production techniques; and 5) integration of carbon fiber operations into a producer's infrastructure.

It has been possible to show the production of dense, graphitic fiber from blends of Kraft lignin and routinely recycled polyolefins or polyesters (24,25). The single fibers, which show proof-of-concept, were produced using low-cost, environmentally friendly melt spinning processes. Melt spinning can be readily integrated as the first step of a carbon fiber production line.

It is likely that a modern production facility for low-cost carbon fiber would include several of the different technologies supported by the Lightweight Materials Program. The microwave-assisted plasma production technologies under development by Paulauskas and coworkers could decrease carbon fiber furnacing emissions, increase production rate, and decrease firing costs by up to 20% (26).

Other technologies, such as pilot to semi-works scale evaluations of mid- and high-temperature gasification technologies for pulp mills, could also facilitate development of a viable, high-volume carbon fiber production infrastructure to support the transportation industry.

CONCLUSION

Current data indicate that it will be possible to produce the quantities of carbon fiber needed for large-scale use in automobiles and light trucks from renewable and recycled feedstocks. Production costs appear to be competitive with industry estimates. The replacement of ferrous metals in passenger transport with lightweight carbon fiber composites would permit the automotive industry to reduce the weight, emissions, and fuel consumption of passenger vehicles.

ACKNOWLEDGMENTS

The support of the Department of Energy, Partnership for a New Generation of Vehicles, Lightweight Materials Program, which supported this research, is gratefully acknowledged. Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Dept. of Energy under contract DE-AC05-00OR22725

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