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Original Article

Characterization of the major reactions during conversion of lignin to carbon fiber

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ABSTRACT

Lightweight design is an essential part of the overall Volkswagen strategy for reducing the CO_2 emissions. The use of carbon fiber offers an enormous lightweight potential. In comparison to steel enabling a mass reduction of up to 70% in automotive parts without a degradation of the functionalities is possible. Today, the use of carbon fiber is limited in mass series applications of the automotive industry by the cost of the conventional C-fiber precursor polyacrylonitrile (PAN). 50% of the cost of a conventional carbon fiber already belongs to the cost of the PAN precursor. Lignin as a precursor for carbon fiber production can realize enormous savings in cost. For qualifying lignin-based carbon fiber for automotive mass production a detailed characterization of this new material is necessary. Therefore, nuclear magnetic resonance spectroscopy and Fourier transform infrared spectroscopy are used. Using the results of these experiments, the major reactions during conversion of lignin to carbon fiber are proposed.

1. Introduction

As of January 1st 2014, all new vehicles are required to meet Euro 6 emission standard. This standard requires all new light passengers and light commercial automotive manufactures to reach an average vehicle carbon dioxide (CO_2) emission of 130 g/km. The average vehicle emission of a light passenger vehicle produced by the brand Volkswagen in 2012 was 130 g/km [1–3].

The emission standards for 2020 have already been determined by the European Union (EU) and by the United States of America Environment Protection Agency (EPA). The next set of regulations been set for both Euro 7 and Tier 3 with an average lightweight vehicle emission of CO_2 of 95 g/km and 114 g/km, respectively [1–3].

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These new emission standards provide a vast amount of challenges for the automotive manufactures. A significant reduction in their vehicle's emissions is necessary to prevent potential fines by the government [1–3].

To meet these onerous regulations, manufactures must focus their resources. For several years the focus was on more efficient powertrains and drivetrains but it is now clear that these emission standards will not be achieve by improvements solely on this. Manufactures must expand their research into fields such as aerodynamics in hopes to reduce overall vehicle drag, and the usage of advance lightweight materials to reduce the overall vehicle's weight.

For automotive manufactures to reach the 95 g CO_2/kg requirement by 2020, the implementation of lightweight constructions cannot solely be based on steel (compare Volkswagen Golf) and aluminum (compare Audi A8) advancements. To accomplish this, a reduction of component weight must exceed 50%. Steel and aluminum can only attribute up to 40% weight reduction [4].

Carbon fiber reinforced plastics (CFRP) can provide this 50% minimum reduction in weight. A weight saving potential of up to 70% on a component without compromising its functionality is possible [4].

For customers of the automotive industry lightweight construction has enormous benefits. In context the reduction of fuel consumption, the increase of the range, as well as a better driving dynamics of the vehicle are the main benefits of lightweight construction using carbon fiber reinforced plastics. For example, the effects of a lightweight construction that reduces the weight of a car by 100 kg, means for the standard engine, a reduction of fuel consumption of 0.3 L/100 km. For an electric drivetrain this would result in a range increase of 100 km [5–7].

However, the weight benefits are currently limited by the high production cost of the carbon fiber. The cost factors are not to be disregarded and one possibility to reduce the cost of carbon fiber is to change the precursor used to produce carbon fiber.

Today the most common precursor used to produce carbon fiber is polyacrylonitrile (PAN). When investigating the cost of producing carbon fiber, it becomes clear that more than 50% of the cost is related to the production of the precursor. The remaining cost is distributed as such: 15% to the oxidation process, 23% to the carbonization process, and the remaining to sizing and spooling [8].

The key to reducing the production cost of carbon fiber is the use of an alternative precursor. The alternative precursors with the highest potential for the automotive industry are polyethylene and lignin.

If lignin is compared to polyacrylonitrile as a precursor for carbon fiber, the ability to reduce the cost of manufacturing is by more than 50% [9]. That's the reason for the investigation of lignin-based carbon fiber in this paper. Lignin is a natural waste byproduct of the paper industry and biorefineries, which is readily available in enormous amounts and due to this very inexpensive. Lignin is also a sustainable, renewable resource. The use of lignin offers significant cost saving potential in the production of carbon fiber. Lignin makes it possible to produce a carbon fiber based on renewable resources.

This paper will show the major reactions, which take place during carbon fiber production from lignin.

2. Experimental

2.1. *Carbon fiber production from lignin*

The following section will show the possibility to make a lignin-based carbon fiber in laboratory scale as performed by the Oak Ridge National Laboratory (ORNL) [4,10]. Five main steps illustrate the use of lignin as a precursor to carbon fiber:

- Washing of lignin powder and drying (**HW**)
- Pelletizing of the lignin powder to pellets (**P**)
- Melt spinning of the lignin fiber (**LF**)
- Oxidation of the fiber (stabilization) (**OLF**)
- Carbonization of the fiber (**CLF**)

At the pulp mill, lignin is dissolved away from the cellulose into black liquor. Then the lignin is precipitated out of the black liquor. After the washing and drying process the lignin powder is obtained.

The twin screw compounding extrusion technology readily reduced moisture and volatiles in the extruded lignin to low and near target levels. Furthermore, using 27 mm extrusion machine, a lignin throughput of 45 kg/h was demonstrated. Semi-production scale lignin pelletizing was also done. A 53 mm diameter extrusion machine equipped with a hot die face cutter was used to successfully pelletize almost 1000 kg of lignin for subsequent melt spinning into precursor fiber.

Using a lab scale machine, "melt blown" spinning was evaluated for producing a lignin fiber web with a filament diameter in the range of 10–20 micron. The fibers were spun into a web approximately 60 cm wide with areal density of 230 g/m^2 at rates approaching 15 kg/h.

Stabilization time was and remains a significant challenge. For the "reference" Alcell® lignin, the stabilization time requires several days. Stabilization must be accelerated to achieve acceptable process economics. A simple tuning of the thermal profile reduced the residence time from ∼150 h to ∼100 h. ORNL stabilized fibers using a ∼100-h batch thermal treatment in a large (>5.5 m^3) oven. 75 kg of lignin fibers were stabilized for further processing. This is the first reported stabilization of lignin fibers at a scale exceeding ∼1 kg.

The stabilized material is carbonized in a furnace under nitrogen atmosphere. It typically operates at 500–1500 degrees Celsius for 5–10 min. Approximately 65% of the material is vaporized during carbonization, with gasses exhausted through an incineration system. The remaining material is nearly 100% pure carbon – a lignin-based carbon fiber. ORNL heat treated the stabilized fibers to produce ∼25 kg of lignin-based carbon fibers. This is the first reported carbonization of lignin fibers at a scale exceeding ∼1 kg.

2.2. *Sample characterization*

For qualifying lignin-based carbon fiber for automotive mass production a detailed characterization of this new material is necessary. Therefore nuclear magnetic resonance