Carbon fiber production: a step-by-step design and market analysis

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Introduction
Carbon fibers (CFs) tend to apply in numerous technological applications, replacing conventional materials (e.g. steel), in forms of composites. Considering their design, various parameters need to be considered. Polymer precursors, such as polycrilonitrile (PAN), lignin, rayon, polyolefin and pitch, are to be selected for carbon fiber production; polymer precursor as raw material has first to be converted into fiber. The main ways to convert a polymer (mainly in powder form) into fiber is wet spinning, dry spinning and melt spinning process. When the fiber formation is achieved, CF synthesis is initiated consisting of oxidation, carbonization and surface treatment steps.

Precursor
Indicative financial data concerning the precursor type are given below [1]. The estimated price for melt spun lignin would be approximately 1.52 $ per kg and in the abstract; the price can be lowered to 1.1 $ per kg. This number is much lower than the proposed cost of other potential precursors such as textile grade PAN at 4.4 $ per kg to 13.2 $ per kg, melt-spun PAN at 6.3 $ per kg and polyolefin at 1.57 $ per kg to 2.36 $ per kg. Taken into consideration the dependence of the petroleum-based precursors from oil price, a possible raise in price would blunt this difference [2]. Table 1 depicts the details of the precursor price and production cost of each precursor type.

<table>
<thead>
<tr>
<th>Material</th>
<th>Precursor Cost (US $)</th>
<th>Production Cost (US $)</th>
<th>Total Cost (US $)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignin</td>
<td>1.52/kg</td>
<td>6.27/kg</td>
<td>7.79/kg</td>
</tr>
<tr>
<td>Polyolefin</td>
<td>1.57-2.36/kg</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Melt-spun PAN</td>
<td>6.3/kg</td>
<td>17.4/kg</td>
<td>23.7/kg</td>
</tr>
<tr>
<td>Textile Grade PAN</td>
<td>4.4-13.2/kg</td>
<td>12.25-25.4/kg</td>
<td>16.65-38.6/kg</td>
</tr>
<tr>
<td>Conventional PAN</td>
<td>11.1/kg</td>
<td>25.15/kg</td>
<td>36.25/kg</td>
</tr>
</tbody>
</table>

Table 1: Cost comparison on different carbon fiber precursors [1]
Source: created by author, with data from D. A. Baker & Rials, 2013; Norberg, 2012

Lignin seems to be a good alternative precursor choice due to its price; however, CFs produced from lignin exhibit poor mechanical properties, when compared with CFs from PAN precursor – (it should be noted that high strength of fibers is not always the engineering property or requirement in the field).

Applications
Aerospace and defense applications have grown significantly and list among the largest consumers of CFs – 13,900 tons, or 30% based on a total of 46,500 tons (Fig. 1). Sport/leisure and wind turbines sector follow in the second place of the list and represent the percentage of 14% on total demand. Automotive segment has shown a great increase in CFs demand in relation to the previous year. More specifically the consumption was doubled and numbered 5,000 tons.
Automotive Focus
The use of carbon reinforced plastics in automotive industry is considered as an important innovation relating to the reduction of CO₂ emissions, lightweight construction and e-mobility and is still on an early stage. The cost of low and standard modulus carbon fibers being appropriate for automotive applications is estimated to be 40 $/kg. The aforementioned are not genuine, because the final price includes the carbon reinforced plastic (CRP) formation stage, so the final price amounts to 95 $/kg. The price for competing materials is 4 $/kg for regular steel, 8 $/kg for high strength steel and 9.5 $/kg for aluminium [1]. According to estimates by the Oak Ridge National Laboratory (ORNL), the ideal price for carbon fiber composite material would be about 11 $/kg accompanied by a tensile strength of 1.72GPa and a modulus of 172GPa. In this case the revenues of carbon fiber market in 2017 for automotive segment could reach the amount of 1.525 million dollars globally. Lignin is a precursor which can deal with these numbers, provided that research will continue in this direction [4].

Spinning Process
The possibility to use lignin as raw precursor was assessed. The lignin was purchased from Westvaco Corp (Indulin AT, MWV). The powder was repeatedly washed with 1M HCl and recovered through porcelain mortar as a fine powder. Subsequently lignin was thermally treated on 160°C under vacuum for 30 minutes. The melt spinning process was performed in two stages: pelletizing of the raw material and spinning the produced pellets.

The stage of pelletizing is given above (Fig.2) and the imported material was a lignin/polymer co-blend, so as to make the raw material spinnable. Poly Ethylene Oxide (PEO) and polypropylene (PP) were chosen to be compound
with Indulin AT. The produced pellets from the previous step were used as feedstock so as to produce fibers with no further treatment. The melt spinning process evidenced that the produced fibers were brittle, not being able to withstand high strain.

Oxidation
Automation and high production rate are the main targets for the design of an oxidation line. The design of appropriate scale-up oxidation apparatus is accomplished, considering a continuous process where a fiber is imported into a four stage oven and can be collected by the take-up system; carbonization process follows (Fig. 4).

Oven
Each level of the multi-oven apparatus is regulated with different temperature and consists of five zones (20 zones totally). Thermal load infliction increases gradually from level to level (approximately 190°C, 220°C, 270°C and
290°C for PAN precursor respectively \[5\]. There is also the capability of gas insertion (air or oxygen) and the removal of resulting gases as well, in each level.

**Panels**

The panels are stainless steel (2mm thick) constructions for godets and motors. The apparatus has four panels in total. The first panel holds the bobbin and two godets (before the fiber enters the furnace). The second and the third panel hold six and two godets, respectively. Godets are made from 2mm thick stainless steel and have 150mm diameter. Each pair of godet is driven by inverted asynchronous motor, purchased by Bonfiglioli (60Nm torque, 0.45kW). Different temperature levels imply different tension, respectively. As the temperature increases, the strain enforcement on the chord has to be reduced. This fact means that each pair of godet rotates with different speed. So, the whole system is automatically controlled via Programmable Logic Controller (PLC) system. The tension in each godet level is checked via appropriate sensors. Godets on each pair are not aligned with one another; one of the two godets is laid flat and the other is located on a six degree bending in relation to the other. The last panel holds the bobbin that collects the oxidized precursor ready for the next step (carbonization).

**Procedure cost**

Comparing the cost structure between PAN and Lignin, the biggest difference arises from the cost of the raw material and spinning process. The estimation of 11.1 $ per kg is based on melt assisted or wet spun fiber formation, plus the price of polyacrylonitrile. Melt assisted and wet spinning methods are expensive due to the use of solvents and relatively low processing speed comparing with melt spinning. PAN precursor as aforementioned is expensive and depends on the oil price. The estimated price of lignin at 1.1 $ per kg is based on melt spinning ready lignin from FP Innovations’ Lignoforce® Technology. Like LignoBoost®, Lignoforce® is also designed for Kraft mill and has similar ash content, molecular weight distribution, etc. Since lignin as CF precursor needs further effort and research to be done; only few early adopters have the processing plant installed such as Domtar Corporation. The price at 1.1 $ per kg in the case of lignin is an industry goal \[1\]. The cost breakdown of PAN (both base line and high volume) and lignin-based carbon fiber in terms of the process steps (spinning, stabilization, carbonization, surface treatment and sizing) is given in the chart below. The cost of spinning includes the cost of precursor. The stages of surface treatment and sizing present similar costs and as to the graphitization step, it is not always necessary.

![Figure 5: Cost breakdown for PAN and Lignin based carbon fiber in terms of $/kg and % overall cost \[1\]
Composites

The growth trends observed in the carbon fiber and carbon composite markets are very similar. In 2013, the demand for carbon fiber reinforced plastics (CRP) was around 72,000 tons, an increase of 9.1% compared to the previous year. The forecast concerning on CRP consumption growth, presents a continuous annual rate of 10.6% until 2020. Although carbon, ceramic and metal matrix materials are used in special applications, the focus of the following section will be primarily on CRP. In 2013, carbon composites generated total revenues of approximately 14.7 billion dollars, of which CRP accounted for 9.4 billion dollars (Fig 6). Composites based on a polymer matrix were therefore responsible for 64% of revenues [3]. The matrix polymers used in CRP production can be further divided into thermoplastics and thermosetting plastics. Thermosetting plastics continue to be the polymer matrix used most commonly with carbon fiber. This is also reflected in the revenue shares of these two polymer types in the total revenues for CRP.

Figure 6: Carbon composites revenues in billion US $ by matrix material [6] Source : created by author, with data from Acmite Market Intelligence 2014

Considering the polymer matrices, the manufacturer takes into account that thermosetting materials present enhanced mechanical properties, low moisture absorption, temperature resistance and reduced material cost. On the other hand thermoplastics offer advantages dealing with high damage tolerance, short processing times, ease on storage and recycle and additional the form and weld well [6].

Recycle Perspective

Production procedure of CFs requires a large sum of money, from raw materials to energy cost while converting the polymer base into carbon fiber. The resale of reclaimed fibers opens the door for an economically interesting business. Pyrolysis is a procedure by which recycle becomes possible [8]. The composite material is heated at around 450°C-700°C, so the epoxy resins can be burned off and the fibers are reclaimed. This technique demands only a 5% of the energy that the original manufacturing process does. Pyrolysis however, presents some drawbacks. The end result is not a fiber of the same length as the original and this fact limits their use to non structural parts. Like, when paper is recycled, the resulted fibers get shorter and shorter and as a result, the strength of the recycled material reduces. This follows from relative surveys funding by Boeing Corporation. Except pyrolysis, recycle of carbon fiber can be performed with a method based on a wet chemical degradation of the polymer matrix, without reducing the strength of the fiber. Reclaimed fiber and processing liquid are separated by using a centrifuge. The liquid is reused for further batches and the fibers receive a water rinse. Some toughening agents and sealers which remain unaffected by the wet chemical process are removed by a final thermal treatment [9].
Acknowledgments
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