DEVELOPMENT OF CONTINUOUS SOLVENT EXTRACTION PROCESSES FOR COAL DERIVED CARBON PRODUCTS

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ABSTRACT

The purpose of this DOE-funded effort is to develop continuous processes for solvent extraction of coal for the production of carbon products. These carbon products include materials used in metals smelting, especially in the aluminum and steel industries, as well as porous carbon structural material referred to as “carbon foam” and carbon fibers. Table 1 provides an overview of the major markets for carbon products. Current sources of materials for these processes generally rely on petroleum distillation products or coal tar distillates obtained as a byproduct of metcoke production facilities. In the former case, the American materials industry, just as the energy industry, is dependent upon foreign sources of petroleum. In the latter case, metcoke production is decreasing every year due to the combined difficulties associated with poor economics and a significant environmental burden. Thus, a significant need exists for an environmentally clean process which can used domestically obtained raw materials and which can still be very competitive economically.

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1.0 EXECUTIVE SUMMARY

The purpose of this DOE-funded effort is to develop continuous processes for solvent extraction of coal for the production of carbon products. These carbon products include materials used in metals smelting, especially in the aluminum and steel industries, as well as porous carbon structural material referred to as "carbon foam" and carbon fibers. Table 1 provides an overview of the major markets for carbon products. Current sources of materials for these processes generally rely on petroleum distillation products or coal tar distillates obtained as a byproduct of metcoke production facilities. In the former case, the American materials industry, just as the energy industry, is dependent upon foreign sources of petroleum. In the latter case, metcoke production is decreasing every year due to the combined difficulties associated with poor economics and a significant environmental burden. Thus, a significant need exists for an environmentally clean process which can used domestically obtained raw materials and which can still be very competitive economically.

Continuous processes using solvent extraction of coal offers the potential to accomplish all of these objectives. Initial proof of concept had been achieved via the DOE-sponsored Consortium for Premium Carbon Products from Coal (CPCPC) which in 2002 demonstrated an all-coal-derived anode with West Virginia University, Alcoa and Koppers. Test anodes produced in this program surpassed all technical requirements as specified by Alcoa. Similarly, very high performance coke, pitch, composites, foams and fibers were demonstrated in DOE-sponsored efforts such as Production of Foams, Fibers and Pitches Using a Coal Extraction Process (DE-FC26-01NT41359).

In 2002-2004, as a result of DOE sponsorship of efforts such as Production of Carbon Products Using a Coal Extraction Process (DE-FC26-02NT41596) modified solvent extraction processes were developed using low cost coal oils in place of more expensive solvents, which preserve high quality of the pitches and cokes produced. At the same time the weight fraction of coal which could be dissolved in solvent was increased from about 0.60 to 0.85 or higher. The solvent/coal ratio by weight was lowered from about 10 to 2, and with recycling a ratio of 0.15 was demonstrated. By synthesizing the solvent from coal, elimination of makeup solvent completely is achievable. From the standpoint of materials balance, commodity feedstock material costs were shown to be less than half the price of the final products, illustrating the potential for profitability.

The main remaining issue is processing cost. Continuous processes will be sought as replacements for batch processing. In addition, processing steps need to be simplified, so that they are comparable to standard processes used at chemical refineries and elsewhere.

Table 1. Estimated Domestic and World Markets for Carbon Products.[1]

Product	Feedstock	Domestic Annual Sales, Tons	Worldwide Annual Sales
Binder Pitch	Coal Tar Pitch (coke ovens)	900,000	1,500,000

Impregnation Pitch	Petroleum Pitch Coal Tar Pitch	200,000	380,000
Mesophase Pitch	Petroleum Pitch Coal Tar Pitch Naphthalene	Negligible	3700
Anode Coke	Petroleum Pitch Coal Tar Pitch	2,000,000	8,000,000
Needle Coke	Petroleum Pitch (US) PP + CTP (Japan)	400,000	1,300,000

The carbon fiber market is primarily served by polyacrylonitrile (PAN) fibers. The total market is approximately 5000 tons worldwide with perhaps 10-15% of that market being served by pitch–derived fibers. Of that market, virtually all is produced using petroleum pitch, with coal pitch contributing insignificantly to the total.

Carbon foam is a relatively new structural material, providing excellent crush resistance and moderate strength and modulus. Carbon foam can also find use as a thermal insulator. Although carbon foams have been fabricated using a variety of processes in the past 20 years, the high processing costs have limited its use in industry. Estimates are not available in the literature, but it is believed that the current worldwide market is probably only a few tons per year. Yet, if the price can be dramatically reduced, it is believed that carbon foam could represent a significant growth product, finding applications for automotive impact protection, naval ship structures, building infrastructure and so on.

2.0 EXPERIMENTAL

Binder pitch is used to produce carbon materials for the metals smelting industry. In particular, the aluminum industry reduces aluminum ore in an electrochemical process utilizing carbon anodes. Binder pitch is used as a “glue” to combine anode grade coke.

Binder pitch is a material used, along with anode coke, to make solid carbon anodes for the aluminum industry. The binder pitch fuses the anode coke to hold it together so that it can be baked into a monolithic form. Approximately 0.4 pounds of carbon are consumed in order to make a pound of aluminum. Binder pitch is also used to produce electrodes for arc furnaces for the steel industry (see figure 1) and also is used for materials composites and other miscellaneous purposes.

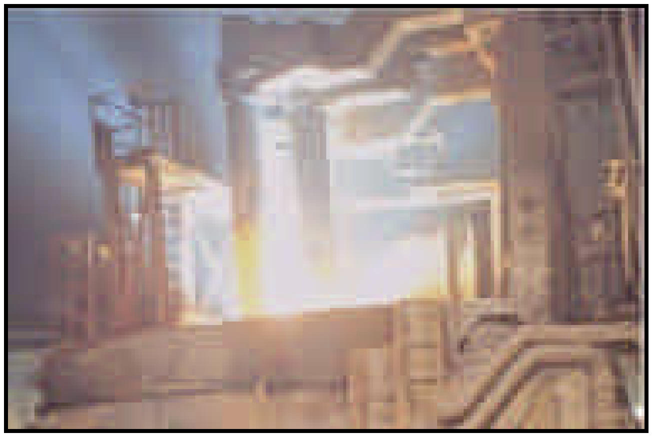

Figure 1. Arc furnaces for steel smelting use graphite electrodes, comprised mainly of binder pitch and premium-grade coke referred to as "needle coke." Photo: courtesy Graftech.

Binder pitch is currently produced as a byproduct of metallurgical coking ovens. These facilities produce metallurgical coke ("metcoke") by heating coal to remove volatile gases. Metcoke functions as a chemical reducing agent as well as a fuel source for steel blast furnaces. The volatile gases from the metcoke production process are collected in the form of a tar. This tar is refined by distillation into several products, including coal oils and coal tar pitch. The coal tar pitch, with some additional processing, is used as binder pitch. An approximate breakdown of the composition of coal tar and coal tar pitch is shown below.

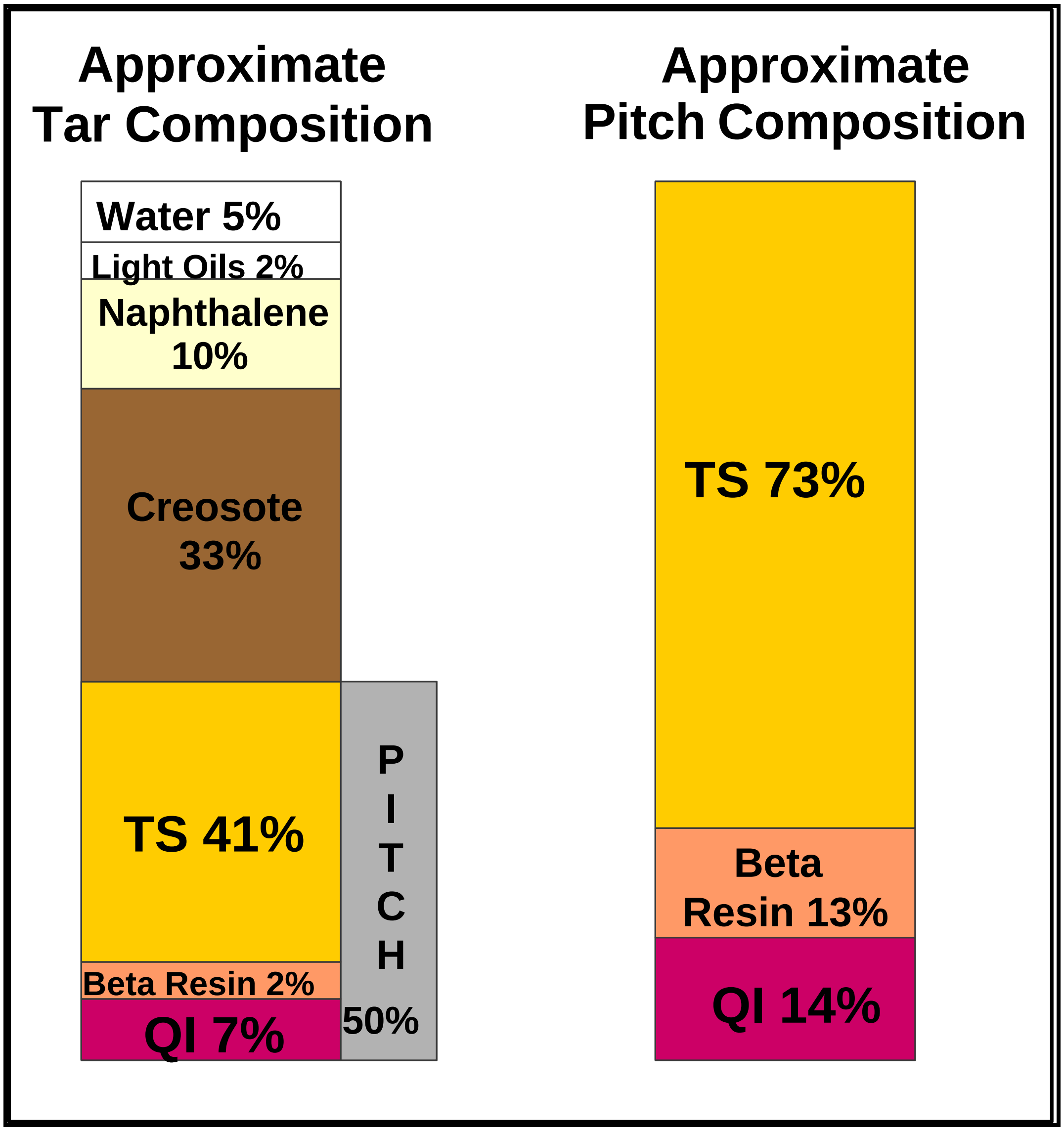

Figure 2. Approximate Composition of Coal Tar and Coal Tar Pitch. Note: QI = Quinoline Insolubles. TS = Toluene Solubles. Beta resin is composed of chemicals insoluble in toluene but soluble in quinoline. Courtesy Koppers.

The supply of binder pitch in the US has been steadily decreasing over the past decades, as shown in Figure 3 below. One of the main reasons is it is a commodity business with small profit margins. In addition, there is an environmental burden created by coking coal to create metcoke, which has decreased the attractiveness of producing metcoke and consequently the coal tar byproduct. If new coke ovens are built in the US, they will likely combust nearly all of the volatiles to produce energy, with excess energy being used to produce electricity (referred to as a “non-recovery metcoke oven”). Thus these newer ovens will not offset losses in coal tar production elsewhere.

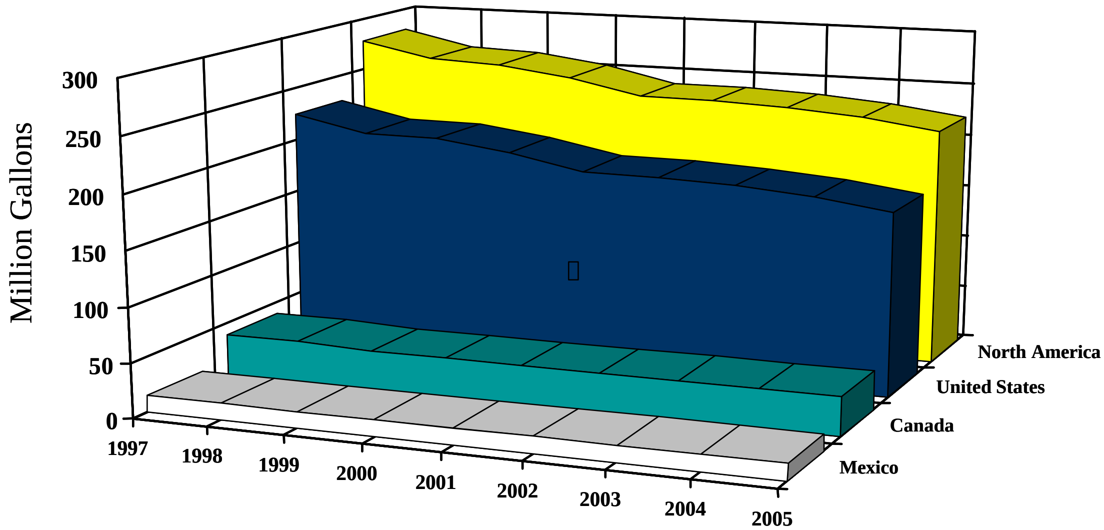

Figure 3. Koppers Industries estimates that binder pitch production will continue to decrease, despite increases in demand.

Despite the decreases in domestic coal tar pitch production, the market for binder pitch is likely to remain approximately constant, as shown by the figures in Table 2. Since only about half of the needed coal tar is produced in the US, industry must turn to other solutions. Pitch suppliers are seeking alternative supplies of binder pitch, including blends of petroleum pitch with coal tar pitch. Increasingly, American industry is forced to import significant quantities of binder pitch from overseas sources, many of which are willing to tolerate adverse environmental impact in order to satisfy excess demand.

Table 2. Koppers Industries Estimates of Binder Pitch Consumption

	1995	1997	1999	2001	2003
Aluminum Industry	597	666	708	679	701
Commercial Carbon	95	95	95	95	95
Miscellaneous	140	127	118	91	91
Total	832	888	921	865	887
Crude Tar Required	1,602	1,711	1,774	1,666	1,706
Crude Tar Available	1,316	1,302	1,077	990	929
Tar Deficit	286	409	697	676	777

Hence, American industry is looking for alternate solutions. Because of the huge amounts of coal available in the United States, it makes sense to consider alternate production strategies for raw materials to satisfy domestic needs for this crucial raw material.

3.0 RESULTS AND DISCUSSION

Anode coke is used mainly by the aluminum smelting industry. Because aluminum is produced by electrochemically reducing the oxide form; i.e.,

$$Al_2O_3 + C \rightarrow Al + CO_2 \quad ,$$

about 0.4 pounds of carbon must be consumed for each pound of aluminum produced. However, over the past decade, as US sources of crude petroleum are increasingly difficult to obtain, petroleum producers are switching to less desirable sources of petroleum. Consequently, the average content of impurities such as nickel, sulfur, and vanadium is increasing on a year-by-year basis. Thus, metals smelters are increasingly driven to foreign suppliers of coke. Just as the case with the pitch industry, the long term decline in production can only be reversed if an environmentally sound process with competitive economics can be developed.

Projected major milestones are as follows:

1. 1Q04: Addition of a wiped film evaporator in the solvent extraction facility.

2. 1Q04: Demonstration of ultrasonic mixing using hydrogen donor solvents and coal slurries.

3. 2Q04: Addition of a continuous Coal Feeder for the Continuously Stirred Tank Reactor in the Solvent Extraction Pilot Plant.

4. 2Q04: Synthetic Pitch specifications established for fibers, foams, cokes and

5. 3Q04: Trial production of carbon foam and fibers using synthetic pitch feedstocks produced from continuous production.

6. 4Q04 Synthetic binder pitch for carbon anodes manufactured according to specifications.

4.0 CONCLUSION

A slow financial expenditure rate is anticipated until the completion of DE-FC26-02NT41596, scheduled for 30 June 2004.

The faculty team consists of the PI, Elliot Kennel, as well as Professors Dady Dadyburjor, Joseph Shaiewitz, Peter Stansberry, Alfred Stiller, Robert Svensson (visiting faculty from Chalmers University in Goteborg, Sweden) and John Zondlo. Teaching faculty contribute their time as cost-share during the academic year. Post-Docs are Philip Biedler and Chong Chen. Technicians include Michael Bergen, Mitchell Clendenin, Jason Hissam, Nathan King, Anthony Oladjide, Morgan Summers and Kevin Whiteman. Three of the technicians are pursuing graduate degrees in Chemical Engineering, with one technician pursuing an MS degree in Mechanical Engineering, one pursuing a PhD in engineering, and two others pursuing MBA degrees. Full-time graduate Students include James Bowers, Steve Carpenter, Lloyd Ford, Manoj Katakdaunde, Madhavi Nallani Chakravartula, and Abha Saddawi. In all, two graduations are expected this summer, and four more by the end of fall semester. In summer 2004, ten students will be supported as hourly employees with the expectation that about half will transition to graduate student or technician status.

Based on these rates it is projected that the first incremental funding of $1.2 MM will be spent by about November 2004.

5.0 REFERENCES

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[1] The Carbon Products Industry Vision for the Future, Industries of the Future, Carbon Products Consortium, WVU-NRCCE, P.O. Box 6064, Morgantown, WV 26506.