ALTERNATIVE BINDER PITCHES FOR CARBON ANODE PRODUCTION

Uthaiporn Suriyapraphadilok, Colin Jennis-McGroarty, Adam Zel, and John M. Andresen
The Energy Institute, Pennsylvania State University
407 Academic Activities Bldg., University Park, PA 16802

Corresponding author e-mail address: jma13@psu.edu

Introduction

Carbon anodes are manufactured from calcined petroleum coke, butt fillers and coal tar pitch. Since the demand of the coal tar pitch in the aluminum industry accounts for about 75% of the pitch market [1] and the production of coal tars is rapidly decreasing in the United States as well as throughout the world [2], the development of alternative binders were considered in this work. Coal tar binder pitches are traditionally obtained from coal tars that are the by-product of bituminous coal coking process used to make coke for blast furnaces in iron production. During the manufacturing of carbon anodes coal tar pitch is mixed with calcined petroleum coke, where petroleum coke is the by-product from the delayed coker in a refinery. Remaining parts of spent anodes from the aluminum production, namely butts, are also crushed and used as filler [3].

This work is focused on the development of alternative binders from various sources of pitches, namely, petroleum pitch (PP), coal-extracted pitch (WVU), and gasification pitch (GP). Petroleum pitch is a residue produced from heat-treatment and distillation of petroleum fractions. A production of coal-extracted pitch involves a prehydrogenation of coal followed by extraction using a dipolar solvent. Gasification pitches are distilled by-product tars produced from the coal gasification process. Each alternative pitch was mixed with a standard coal tar pitch (SCTP) at various mixtures and laboratory-scale test anodes were formed and studied.

Experimental

Materials: Four types of pitch were used in this study: two standard coal tar binder pitches (SCTP-1 and -2), a petroleum pitch (PP), a coal-extracted pitch (WVU-5), and a gasification pitch (GP-1). The properties of each pitch are summarized in Table 1. Petroleum coke and recycled anode butts were crushed and aggregated into three different sizes: (i) Fines: >200 Tyler mesh size; (ii) Intermediate: 60-200 Tyler mesh size; and (iii) Coarse: <60 Tyler mesh size

Compositions: All experimental-scale anodes in this work were made using the following compositions:

Pitch:Butt:Coke = 22:29:49

Fine:Intermediate:Coarse = 40:35:25

Table 1. Properties of pitches.

Property	SCTP-1	SCTP-2	PP	WVU-5	GP-1
Softening Point (°C)	112.5	111.9	111.9	112.2	115
Quinoline Insolubles (wt%)	13.6	15.9	0.1	N.A.	<0.1
Toluene Insolubles (wt%)	27.8	30.9	3.2	N.A.	N.A.
Coking Value (wt%)	N.A.	57.9	47	50.3	N.A.
Ash Content (wt%)	N.A.	0.29	0.08	0.2	N.A.
Specific Gravity @ 25°C	N.A.	1.34	1.246	1.25	N.A.

N.A. = Not Available

Mixing and Forming: The aggregate fillers and binders, which weighed about 15 grams in total, were mixed at about 50°C above the softening point of the pitch mixture. The CARVER cylindrical mold with an inside diameter of 28.58 mm was preheated to about 10°C above the softening point of the pitch mixture. The hot mix was placed into the mold and rapidly pressed at 9,000 psi for 2.5 minutes. The final green anode was cylindrical in shape with typically 28.60 mm. in diameter and 13.00-14.00 mm in height.

Baking: The green anodes were baked with a low heating rate to about 1075°C over a period of 5-6 days prior to cooling. The temperature profile was 25°C/hr from 25°C to 125°C; 3.5°C/hr from 125 to 575°C; 100°C/hr from 575 to 1075°C; hold at the temperatures between 950 and 1075°C for 6 hours; and cool down in the furnace to room temperature.

Properties Measurement: The green and baked anodes were weighed to the nearest 0.001 gram and their dimensions were measured by a caliper to the nearest 0.01 millimeter. The apparent densities of both green and baked anodes were calculated by a ratio of mass and volume. The amount of pitch loss after baking was calculated by assuming that all the weight loss was resulting from the pyrolysis of pitch. Finally, the volume change of the baked anodes relative to the green ones was calculated.

Results and Discussion

Each type of pitch was mixed with the standard coal tar pitch (SCTP) at various percentages while maintaining the total pitch content of 22 wt% for the anode aggregate. Figures 1-3 show the apparent and baked densities of the green and baked anodes, %pitch loss and %volume change of the experimental-scale anodes of the SCTP-2 + PP, SCTP-2 + WVU-5 and SCTP-1 + GP-1 mixtures, respectively. The addition of PP gives an improvement in apparent densities for both green and baked anodes (Figure 1(a)). For PP the green apparent density increases from 1.719 g/cm^3 for the SCTP-2 only to 1.736 g/cm^3 for the PP only, while the baked apparent density increases from 1.542 g/cm^3 for the SCTP-2 only to 1.561 g/cm^3 for the PP only.

However, these trends do not keep up for the addition of WVU-5 and GP-1. The addition of WVU-5 gives slightly poorer densities of the green and baked anodes (Figure 2(a)). The green apparent density of the SCTP-2 + WVU-5 decreases from 1.719 g/cm^3 for the SCTP-2 only to 1.703 g/cm^3 for the WVU-5 only, while the baked apparent density decreases from 1.542 g/cm^3 for the SCTP-2 only to 1.491 g/cm^3 for the WVU-5 only. For GP-1, the green apparent density of the SCTP-1 + GP-1 is quite similar for all pitch ratios and the average green density is about 1.73 g/cm^3, while the baked apparent density decreases from 1.575 g/cm^3 for the SCTP-1 only to 1.487g/cm^3 for the GP-1 only.

The main factor for the reduction in baked density is due to the increased loss of binder during baking as shown in Figures 1(b), 2(b) and 3(b). The pitch loss is defined as a reduction in anode weight over initial pitch content (22%) since the weight loss of the coke material can be neglected. The addition of GP-1 to the SCTP-1 tends to give the highest pitch loss among all three mixtures (Figure 3(b)), while the addition of PP gives a slightly increase in pitch loss compared to the SCTP-2 only (Figure 1(b)). Also, for all SCTP + alternative pitch studied here, the addition of the alternative pitch more likely gives a lower volume change of the baked anodes compared to the baked anodes with SCTP only as shown in Figures 1(c), 2(c), and 3(c).

Of all pitch mixtures studied here, the addition of an alternative pitch shows quite similar trends, i.e. SCTP gives a lower pitch loss and higher volume change compared to the pure alternative pitches. Among all three alternative pitches, the addition of WVU-5 and GP-1 shows poorer properties of the anodes among all three mixtures, i.e. high pitch loss and low baked densities, while the addition of PP shows little impact on the properties of the anodes for most SCTP-PP compositions. The addition of GP-1 and WVU-5 also gives comparable anode properties when the SCTP:WVU-5/GP-1 ratio is greater than 50:50.

Conclusions

The results of this study show that the petroleum pitch offers a potential to be used as additives to the standard coal-tar pitches for use as binders in aluminum anode production, while the addition of coal-extracted pitch and gasification pitch give comparable anode properties when the ratio of standard coal tar pitch and alternative pitch is greater than 50:50. Further work should be conducted to study the causes of improvement of adding alternative pitches to better understanding the roles of the binders from various types of pitches.

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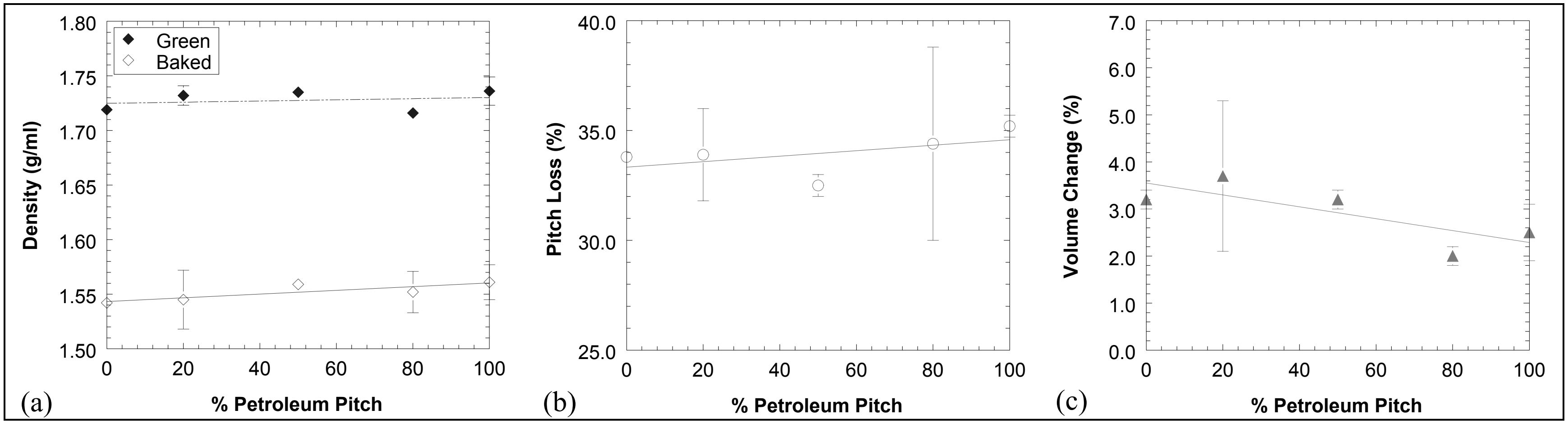

Figure 1. Properties of green and baked anodes of various compositions between SCTP-2 and PP: (a) apparent densities of green and baked anodes, (b) % pitch loss, and (c) % volume change. The error bars show the standard deviations of each experimental set. The dashed lines show the linear relationship of the mixtures.

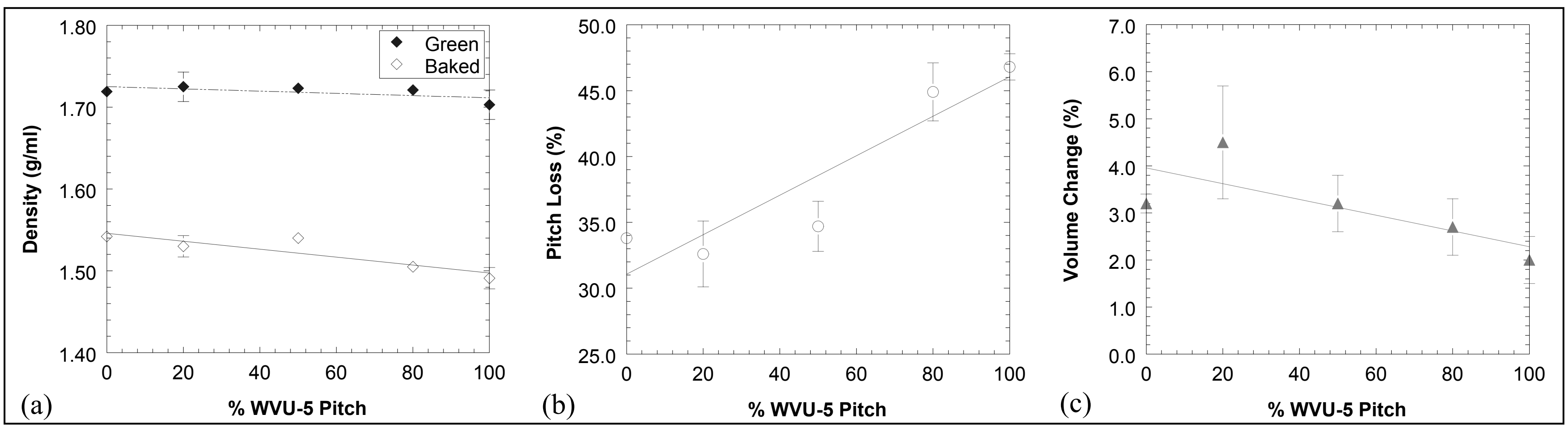

Figure 2. Properties of green and baked anodes of various compositions between SCTP-2 and WVU-5 Pitch: (a) apparent densities of green and baked anodes, (b) % pitch loss, and (c) % volume change. The error bars show the standard deviations of each experimental set. The dashed lines show the linear relationship of the mixtures.

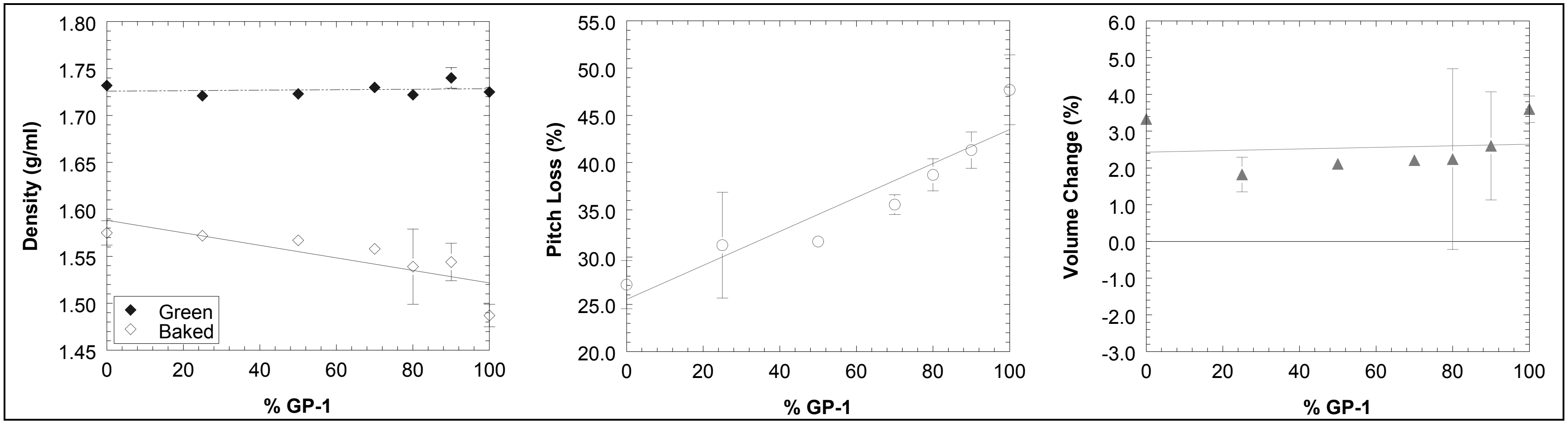

Figure 3. Properties of green and baked anodes of various compositions between SCTP-1 and GP-1: (a) apparent densities of green and baked anodes, (b) % pitch loss, and (c) % volume change. The error bars show the standard deviations of each experimental set. The dashed lines show the linear relationship of the mixtures.