Anhydrous Carbon Pellets – An Engineered CPC Raw Material

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Abstract

The paper reports on a new technology Rain Carbon has been developing to produce an engineered calcined petroleum coke (CPC) product. Agglomeration of green petroleum coke (GPC) fines through either granulation/pelletizing or briquetting can be used to produce a CPC product with improved properties. Pelletizing GPC fines can produce high bulk density pellets hereafter referred to as anhydrous carbon pellets or ACP. ACP densifies when calcined to produce a high bulk density, free flowing CPC product. The spherical particle shape provides improved particle packing densities to irregular shaped CPC particles during anode production. The paper will summarize key results including pilot anode properties showing improvements in baked anode density, electrical resistivity and other properties when using ACP. A key benefit of ACP is the ability to produce a fully engineered CPC product and Rain Carbon is currently working on building a full scale, commercial plant in the US.

Keywords: Petroleum Coke, Calcination, Anode, Density, Agglomeration, ACP

1. Introduction

Agglomeration of fine particle size, bulk solids is a well-established process technology used by many different industries. One of the most well-known applications is granulation or pelletizing of iron ore fines. This is done on a massive scale with some plants producing more than 9 million tons per year. At the other end of the spectrum in terms of volume and product value, is the pharmaceutical industry which typically uses high speed pellet presses to make tablets. Between these two extremes many different agglomeration technologies are used including briquetting, spray drying/granulation and pellet mills which are now routinely used to make wood or biomass pellets for heating and/or power generation [1].

In 2011, Rain Carbon started to experiment with the agglomeration of green petroleum coke (GPC) fines as a way to improve calcining economics. When a rotary kiln is used for calcining, around 10% of the finest particle size GPC becomes entrained in the counter-current flue gas stream inside the kiln. The fines are carried out the back end of the kiln and into a high temperature combustion chamber or pyroscrubber where they are combusted along with any remaining volatile matter (VM). The heat generated in this process is typically recovered and used to produce steam in a heat recovery steam generator (HRSG). Most plants with a HRSG generate electrical power via a steam turbine generator. The sale of power (or steam) is normally an important economic component of the calciner. GPC fines loss is much lower in a shaft calciner (typically <3%) due to the absence of a counter-current flue gas stream [2] inside the calciner.

As GPC prices increase, rotary kiln calciners are incentivized to reduce GPC fines carryover. Since power prices are normally fixed, it is more favorable for a calciner to convert as much GPC to calcined petroleum coke (CPC) as possible. In 2011, low sulfur GPC prices increased dramatically with US Gulf prices hitting US$400/ton in Q3 2011 [3]. The idea to separate out and agglomerate GPC fines using one of the commercially available technologies was conceived during this period. It provides a way to reduce fines carryover and recover the fines as CPC product instead. Granulation to produce spherical shaped pellets was selected as the first technology to evaluate since there are some potential benefits in producing round particles in terms of particle packing density and powder flowability. A recent paper [4] highlights the particle packing benefits of spherical shaped CPC particles.

A second benefit of agglomerating GPC fines is an environmental one. When fine particle size GPC is combusted in a pyroscrubber, any sulfur in the GPC will be fully converted to SO_2 in the flue gas stream. During calcination, all cokes lose some sulfur so the sulfur level of CPC is always lower than the GPC sulfur level. For low sulfur cokes (<2.5 %), the sulfur loss is in the range of ~8-10 % and for higher sulfur cokes, ~11-14 %. The generation of SO_2 via this process is unavoidable and occurs in both rotary kiln and shaft calciners. Fines carryover, which takes place predominantly in rotary kiln calciners, results in a further increase in SO_2 emissions and the higher the GPC sulfur level, the higher the SO_2 emissions via this route. Agglomeration of fines therefore eliminates SO_2 emissions associated with fines combustion. For calciners that scrub SO_2, this will reduce scrubber operating costs and for calciners without scrubbers, it will reduce stack SO_2 emissions.

2. Rationale for GPC Fines Agglomeration

Although agglomeration is a well-known technology, the idea to agglomerate GPC fines was based on an understanding of what would likely happen to these agglomerates during calcination. It was expected that the agglomerated fines would densify and form a calcined product with good bulk density and strength. The agglomeration tendency of GPC has been described previously [5] in relation to its contribution to problems like coke ring formation. GPC fines typically contain a higher volatile matter (VM) content than coarser coke particles due to the heterogeneity of coke formation in the delayed coker. Well-coked material at the bottom of the coke drum has a lower VM and is harder than coke at the top of the drum. When the drum is de-coked with a high-pressure water jet, the softer, higher VM coke breaks down into fines and the coarser, lower VM coke remains in larger coke pieces.

If the fines are agglomerated and heated, the relatively high VM material softens and generates condensable tars which make it sticky. With further heating, these tars undergo cracking reactions which generate lighter hydrocarbon molecules like CH_4 and H_2 [6] which are then combusted in the kiln and pyroscrubber. With further heat treatment, the tars form solid coke which binds particles together in close proximity to each other. This phenomenon also leads to the formation of an agglomerated product from a shaft calciner [2] and is the fundamental basis for the technology development described in this paper. If GPC fines can be agglomerated successfully into a high bulk density precursor, the agglomerate should densify and develop strength during calcining.
Preliminary agglomeration trials were undertaken using granulation/pelletizing equipment similar to that used by ceramic proppant manufacturers [7]. Initial results were encouraging and Rain Carbon filed two patents on the concept in 2011 which were granted in 2013 and 2014 [8,9]. The scale of work done on the project gradually increased after that with the ultimate goal of developing a commercially viable process technology. Rain Carbon is now in the early stages of constructing a plant to make ACP.

3. Initial Results

In the first set of experiments, GPC was screened at a particle size of 2 mm. The -2 mm fines were pelletized using a wide range of binders such as PVA (polyvinyl alcohol), CMC (carboxymethyl cellulose), molasses, dextrin (sugar) and coal tar pitch. Most of the binders worked quite well except coal tar pitch. The GPC had to be heated first to remove the moisture and then heated to calciners. This does not change the coke in any material way. Producing ACP on the other hand, would be a big step towards producing a fully engineered CPC product. The combination of micro-blending with different green cokes and the production of a high bulk density, spherical product can give some significant potential benefits for anode production and performance. CPC made from ACP is also a free-flowing material which can mitigate some of the problems that occur with CPC related to silo segregation effects.

If ACP was adopted as the primary CPC production feedstock, it would be necessary to broaden the particle size distribution to include spherical particles in the size range of 0-2mm. Without a broader size distribution, the poured bulk density or stowage factor of the CPC product would be lower. A CPC product based entirely on 2-10 mm pellets for example, would require more silo storage volume for a given mass than existing CPC material with fines. It is not difficult in principal to make finer particle size pellets but this would require processing changes which would add additional cost. Producing a product with a broader particle size distribution would also reduce the need to crush large amounts of calcined ACP to produce the finer portions of the aggregate recipe.

10. Conclusions

The results presented in this paper show that it is possible produce a better performing CPC product through the agglomeration of GPC fines to make ACP. This will add some additional cost during calcination but the cost can be at least partially offset by reduced fines carryover and higher CPC production per ton of GPC. At higher GPC prices, the economic benefit of making APC increases. The spherical shape of APC gives particle packing benefits which translates together with reduced porosity into an improvement in CPC bulk density and anode properties like baked anode density, electrical resistivity, flexural strength and compressive strength. Production of ACP opens the door for a more engineered approach to producing CPC including the potential to produce a uniform, micro-blended ACP product where all CPC pellets properties are identical. The technology would also eliminate the fines/dusting problem that occurs with shaft CPC. Moreover, ACP also results in a direct benefit to the calciner in reducing SO_2 production.

Rain Carbon is now embarking on a project to build a commercial scale plant in the US to make ACP. Such a plant will allow a full evaluation of the benefits of this new technology for both CPC and anode production.

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