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Original Research Paper

A systematic framework to monitor mulling processes using Near Infrared spectroscopy

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ABSTRACT

The optimal design of sensor location and setup is essential to ensure the accuracy and precision of in-line process monitoring of water/moisture content. This manuscript presents a systematic framework of using Near Infrared (NIR) spectroscopy to monitor moisture content in an alumina mulling process that is commonly used in the upstream operation of catalyst supports production. For this, the optimal conditions of NIR sensor setup and critical quality attributes (CQAs) of a mulling process have been first identified and then calibration models for monitoring moisture at various conditions were developed and validated. The results suggest that there is a strong relationship between sensor setup and prediction accuracy. Therefore, optimal conditions such as operating distance of the NIR sensor, sample thickness and acquisition number need to be identified prior to installment of the sensor into the manufacturing plant. In mulling processes, the particle size distribution (PSD) and surface roughness/smoothness can also vary during operation, making the monitoring of moisture content a difficult task. In this study, the effects of PSD and powder surface characteristics on moisture content measurement has been investigated and it has been found that if suitable raw data preprocessing has been applied, the effect of agglomerate size and sample surface characteristics on the accuracy of the in-line measurements can be significantly minimized. This will allow the use of a single calibration model for a range of PSDs and powder bed smoothness/roughness and that will save a significant amount of time and resources. Here, a mulling process where a microNIR sensor has been used for monitoring of moisture content has been considered as a demonstrative example. However, the approach is generic and can be applied for any combination of process and sensor.

1. Introduction

Inorganic metal-oxide supports offer unique properties for the immobilization of metal complexes, such as mechanical strength, surface area and porosity [1]. Alumina is one such inorganic support which has been widely used for several decades in the catalyst industry with applications in the petroleum [2], petrochemical [3], pharmaceutical [4] industries and biofuels [5]. The presence of the alumina support [5] and even the structure of alumina can significantly affect the performance of catalysts, as indicated by Luo et al. [3].

Catalysts supported on alumina, which are synthesized by ammonia precipitation, exhibit higher activity and selectivity to isobutene than the corresponding catalyst synthesized from hydrochloric acid reflux. Due to its importance, there is a large demand for alumina supports in the catalyst industry. However, the large-scale manufacturing of extrudable alumina with desired particle and pore size distribution, and surface area is still a challenging task in the current catalyst production scenario due to difficulties in handling powders.

Usually, the production of alumina is processed in three steps: mulling, extrusion and calcination. Mulling is similar to granulation but is applied in catalyst manufacturing and incorporates wetting, mixing, primary particle size reduction and particle shaping, all within a single unit operation. It improves flowability, reduces dustiness and increases bulk density. Moreover, several highly favored properties including high porosity and large surface area, which brings about faster reaction rates, are introduced by mulling. This effect is achieved by decreasing primary particle size with the help of peptizing agents and high shearing action. A well-mulled paste after undergoing extrusion, to gain the desired shape, is subsequently calcined. The process of calcination removes any residual moisture and mainly volatile fractions leaving behind

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pores in these alumina supports that allow for the impregnation of catalyst. A set of process variables, namely temperature, moisture content, pH, impeller speed and chopper speed, are known to affect the quality of the final product [6–8]. Therefore, it is a challenging process to optimize and scale up based on the process variables alone. Extrusion is a commonly used shaping process in many industries, as well as in the catalyst industry, since extruded catalyst supports are much easier to handle and recycle. The main condition that the extruded materials have to fulfill is having sufficient plasticity [9]. Alumina is a non-plastic material and, therefore, extrusion of alumina pastes requires processing additives such as binder and lubricant agents to impart plasticity and flow characteristics, which is another reason for the need of mulling in catalyst support production. In the mulling process, water, with the possibility of a peptizing agent such as nitric acid, can be used as the binder, wherein the binder to solids ratio has significant effect on the plasticity. This makes the monitoring of water/moisture content extremely important. Much less attention however has been paid to the monitoring of this moisture content.

Generally, batch processing is a commonly used method since the machinery for batch production is already installed and is more flexible, in terms of both machine application and productivity adjustment. However, continuous processing is more popular since it helps with stabilization of product quality as well as reduction of manufacturing time and cost of goods. It has been well established in the chemical, cosmetics and food industry [10–12]. For continuous process monitoring, non-destructive monitoring techniques are generally used, especially vibrational spectroscopic methods such as Near Infrared (NIR) and Raman, which are combined with multivariate calibration routines for use as in-line process analyzers [13–15]. These monitoring techniques offer several advantages over conventional wet chemistry techniques including non-invasiveness, little or no sample preparation and rapid measurements [16,17]. Recent examples where process monitoring has been utilized include raw material dispensing, chemical reactions, granulation, drying and powder blending [18–24]. Similarly, a PAT (process analytical technology) based monitoring is illustrated from an industrial perspective by Chandra et al. [25]. Moreover, several works also incorporate NIR for feedback process control [26,27]. All of these applications show unique advantages and feasibilities of using vibrational spectroscopy as real time PAT tools.

The –OH stretching vibration is a very strong absorption band in the NIR region and is thereby used for water content measurement, resulting in the successful use of NIR in food and chemical manufacturing [15,28–30]. Analysis of samples in the form of solids, liquids and pastes are simpler using NIR as sample preparation is minimal. Since moisture content plays a key role in the mulling process, this paper discusses the use of NIR as a suitable PAT tool in process monitoring. During the mulling process, material characteristics such as particle size distribution and powder surface properties such as smoothness and roughness could slightly vary. The effect of these variations on the moisture content measurement is still an open area of research. Accuracy and precision of measurement also significantly depends on the location and installment of the sensor into the manufacturing plant. Therefore, prior to sensor integration, optimal conditions such as sensing location distance between sensor and sample, characteristics of sensing interface, and data acquisition specifications need to be identified. However, because of the unavailability of a systematic method, the identification of the optimal sensor conditions is still based on a heuristic approach.

Critical operation parameters of the NIR spectrometer such as scan number, acquisition time, distance between sample and detector, sample thickness and sensor locations in order to obtain accurate measurements have been identified in this study. The effect of particle size and water content of the particles on NIR measurements have also been investigated since they change the physical properties of material surface which would impact the NIR absorption. The methodology discussed is generic and can be used for any combination of process and PAT tools.

2. Experimental details

2.1. Materials and equipment

A specific grade of alumina, CATAPAL boehmite alumina, was used in this study, which was manufactured by Sasol, and the distilled water was generated by a Millipore Milli-Q Water Purifier.

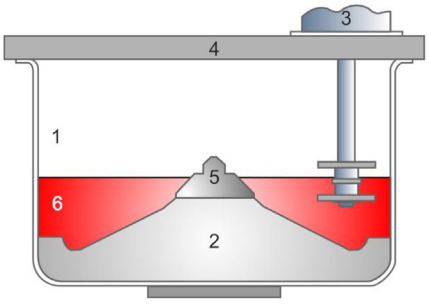
A Design of Experiment (DOE) analysis was performed using the Minitab 16 statistical software. For the calibration model, the alumina and water were mixed in a vortex mixer from VWR International. The batch mulling experiments were carried out in a KG-5 high shear granulator from Key International, Inc. and the continuous mulling took place in a 2″ continuous processor from Readco Kurimoto, LLC. The NIR chosen for this purpose was a MicroNIR 1700 spectrometer from JDSU measuring diffuse reflectance in the wavelength range between 950 and 1650 nm. IRSE-XP software from JDSU was used as the spectral interface. Processing the spectral data subsequent analysis was carried out by Unscrambler X from CAMO Software Inc.

2.2. Batch mulling process

It is necessary to know the end-point in mulling since it reduces the possibility of over wetting and over agglomeration and saves energy and time on the other hand. Water distribution, which is a measure of uniformity, could be used as an indicator in determining the end-point of the process. To allow for a better understanding of the water distribution range being investigated, when discussing batch mulling experiments, solid:liquid (S/L) ratio has been used for indicating the formulation being granulated. During NIR measurements, since moisture is being monitored, water content in the sample (or % LOD) is mentioned.

The experimental setup for a batch mulling process is shown in Fig. 1.

The mulling process can be divided into three stages. The first stage is the de-agglomeration stage, where, lumps of powder are broken down at a low impeller/chopper speed, 150/500 rpm for two minutes. Next, during the liquid addition stage (which is approximately 5.65 min), a flow of 65 ml/min is maintained and the impeller/chopper speed is gradually increased. Then, the process moves into the third stage i.e. maturation. In the maturation stage, the impeller/chopper speed is set at a higher



1 – stainless steel bowl (volume 3.9 L), 2 – three-blade impeller, 3 –chopper, 4 – impact resistant cover, 5– safety screw, 6 – batch

Fig. 1. Experimental setup for a batch mulling process.