Pet. Sci. (2016) 13:782–787
DOI 10.1007/s12182-016-0118-1

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ORIGINAL PAPER

Effects of pH on rheological characteristics and stability of petroleum coke water slurry

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Received: 10 February 2016 / Published online: 3 October 2016

Abstract In this study, the effects of pH on slurrying properties of petroleum coke water slurry (PCWS) were investigated. The slurrying concentration, rheological characteristics and stability of PCWS were studied with four different types of additives at pH varying from 5 to 11. The results showed that the slurrying concentration, rheological characteristics and stability of PCWS all increased at first and then decreased with increasing pH from 5 to 11, and a pH of around 9 was found to be the most favorable acid–alkali environment to all these three slurrying properties. It was also indicated that only in a moderate alkaline environment can the additives be active enough to react with particle surfaces sufficiently to obtain good slurrying concentration and form a stable three-dimensional network structure, which can support strong pseudoplastic characteristics and good stability. An acid environment was a very unfavorable factor to the slurrying properties of PCWS.

Keywords Petroleum coke · Petroleum coke water slurry · pH · Slurrying concentration · Rheological characteristics · Stability

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Edited by Xiu-Qin Zhu

1 Introduction

Petroleum oil and its products are important fuels and chemical raw materials, which are widely used in almost all aspects of production and life. Along with the rapid development of the economy, the demand for petroleum oil keeps increasing (Hu 2014). More and more petroleum coke, as an end product of the petroleum refining process, is produced (Ren et al. 2012; Zhang et al. 2012). Petroleum coke, with its characteristics of high carbon content, high calorific value and low ash content, has become a popular fuel for power generation (Chen and Lu 2007; Milenkova et al. 2005; Anthony et al. 2001; Wang et al. 2004; Sheng et al. 2007) and has started to become a potential gasification fuel (Valero and Usón 2006; Fang et al. 2005).

With the development of coal water slurry (CWS) technology, increasing attention has been paid to petroleum coke water slurry (PCWS). CWS and PCWS are liquid fuels of low pollution and high efficiency and can be pumped like oil by pipeline and burned in power plants as an oil substitute (Zhan et al. 2010). They change the traditional combustion of solid fuels and show huge environmental protection and energy-saving advantages (Cen et al. 1997; Wu et al. 2015). Because of the strong hydrophobicity, PCWS generally possesses higher solid concentration than conventional CWS. Moreover, PCWS also can be a superior raw material for industrial gasification (Gao et al. 2012a, b; Zou et al. 2008). Hence, PCWS has become an important way to utilize petroleum coke efficiently and cleanly.

The slurrying properties are most important for industrial application of the slurry fuels. The solid concentration of the slurry fuels should be increased as much as possible to reach a high level of heat value and thus ensure efficient gasification and combustion, but the viscosity should be low enough to facilitate preparation, pumping and atomization of the slurry. Many studies are aimed at influencing factors on PCWS's slurrying properties (Gao et al. 2012a, b; He et al. 2011; Xu et al. 2008; Vitolo et al. 1996; Wang et al. 2006). Yet, up to now, the effect of pH on slurrying properties of PCWS is rarely reported. Acid–alkali properties of the slurry can directly influence the interactions between the additives and the surface of petroleum coke particles and subsequently influence the slurrying properties of PCWS. In this work, the effects of pH on the slurrying properties of PCWS were investigated.

2 Materials and methods

2.1 Material

A petroleum coke from America was used in the experiments. The proximate and ultimate analysis results of the petroleum coke used in this work are shown in Table 1. The petroleum coke was ground in a ball mill to obtain the pulverized sample, and particles below 149 µm were selected by an electric sieve shaker to prepare PCWS. The granularity distribution of the selected petroleum coke particles was analyzed with a Mastersizer 2000 Granularity Meter (Malvern, UK), as shown in Fig. 1. The average particle diameter was approximately 27 µm.

Chemical additives are an important component of slurry fuel, for they can help particles to disperse stably in the slurry. Four kinds of anionic surfactants were used as additives in PCWS preparation in this work. These were sodium methylene naphthalene sulfonate-sodium styrene sulfonate-sodium maleate (NDF), methylene naphthalene sulfonate formaldehyde condensate (MF), lignin sulfonate (LS) and petroleum sulfonate (PS). The additive dosage was fixed at 0.8 wt% based on dry petroleum coke (Gao et al. 2015).

Table 1 Proximate and ultimate analysis results of petroleum coke

Issues	Results (air-dried basis)
Proximate analysis, wt%	
Moisture	1.24
Ash	0.85
Volatile	11.68
Fixed carbon	86.23
High heating value, kJ kg^{-1}	35,146
Ultimate analysis, wt%	
C	85.57
H	4.01
N	1.84
Total S	3.54
O	5.04

The oxygen datum was obtained by calculation

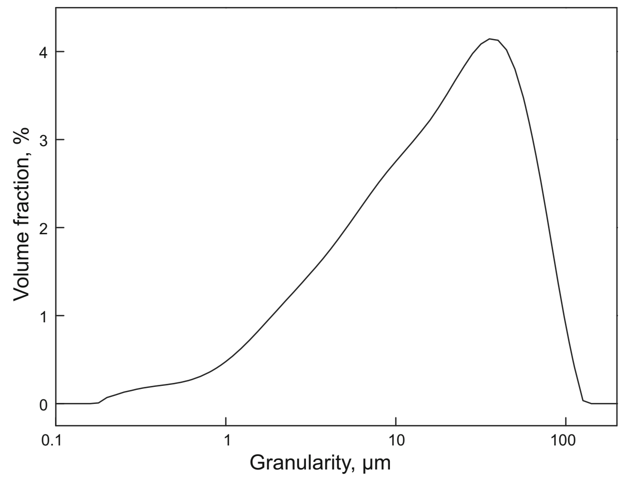

Fig. 1 Granularity distribution of petroleum coke particles

2.2 Methods

The petroleum coke particles, deionized water, one additive and moderate HCl or NaOH were mixed with an electric mixer at 1000 r/min for 10 min to form a PCWS sample. With each additive, PCWSs were prepared at four different pH values (i.e., pH 5, 7, 9 and 11). The pH values were measured by using an E200 Portable pH Meter (Mont, China).

The apparent viscosity and rheological properties of PCWS were measured on a rotary viscometer (NXS-4C, China). A PCWS sample was first loaded into the viscometer, and then the shear rate was increased from 10 to 100 s^{-1}. The relationship of the shear stress and the shear rate can be revealed in this process. Keeping the shear rate at 100 s^{-1} for 5 min, the apparent viscosity data were recorded every 30 s during a 5-minute period. The average apparent viscosity at 100 s^{-1} was calculated from the ten apparent viscosity values recorded. During the entire process, temperature was controlled at 20 ± 1 °C.

The solid concentration of PCWS was determined by drying the slurry in an oven at 105 °C for 2 h and then weighing the dried residue.

Measurement of stability of PCWS was taken after the slurry was sealed in a container for 7 days. In order to ensure the reliability of the experimental results, the stability of PCWS was measured by both the rod-insertion method (Zhao 2009) and a visual method (Li et al. 2008). In the rod-insertion method, a steel rod was inserted vertically and freely from the slurry surface, and the first traveling length through the slurry was recorded. Then the steel rod was strongly pressed down to the bottom of the container, and the second traveling length through the slurry was recorded as well. The relative height of the hard sediment layer can be obtained by calculation, which is an index to evaluate slurry stability. A large relative height of hard sediment layer indicates poor stability of the PCWS. In the visual method, the changes in slurry properties, such as separated water, could be found through observation. The mass ratio of separated water to total slurry is used to evaluate the stability of slurry. A higher water-to-slurry ratio indicates a worse stability.

3 Results and discussion

3.1 Effects of pH on slurrying concentration of PCWS

Solid concentration at a specific viscosity of 1000 mPa s with the shear rate of 100 s^{-1} is used to evaluate the slurrying concentration of petroleum coke. The higher the solid concentration, the better the slurrying concentration of petroleum coke (Hu et al. 2009). Figure 2 shows the relationship of slurrying concentration of PCWSs (with different additives) with pH.

Figure 2 shows that the slurrying concentration increased first and then decreased with increasing pH and that an acid environment of pH 5 resulted in the worst slurrying concentration and an alkaline environment of pH 9 resulted in the best slurrying concentration. The reason is that the additives themselves possess moderate alkalinity, and the activity of the additives can be restrained in acid or strong alkali conditions, leading to the dispersion of particles worsened and slurrying concentration decreased.

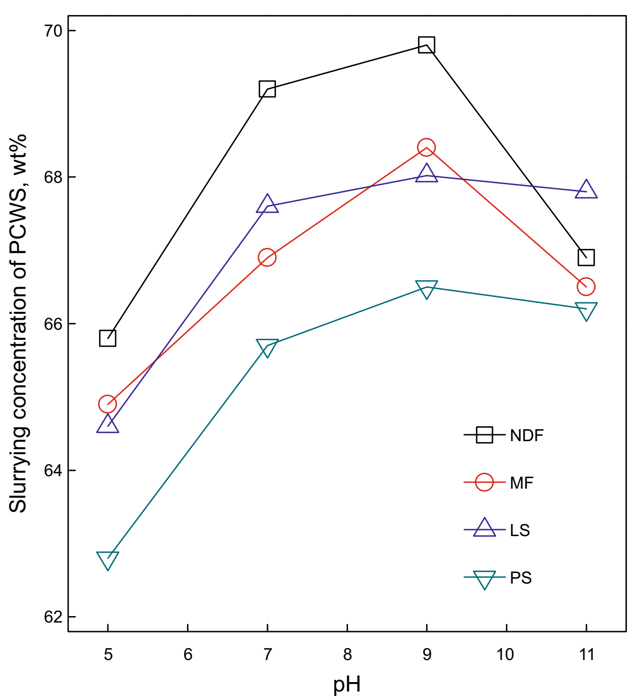

Fig. 2 Effects of pH on slurrying concentration of PCWS

3.2 Effects of pH on rheological characteristics of PCWS

Rheological characteristics are very important to the industrial application of slurry fuels. These are not only related to the slurrying properties, but also directly affect the pumping, atomizing and combustion performances of the slurry fuels (Ma et al. 2012, 2013a, b; Li et al. 2010; Meikap et al. 2005; Chen et al. 2009). Usually PCWS is expected to be of high viscosity to promote stability during storage and low viscosity to ensure fluidity during transport; hence, "shear-thinning" pseudoplastic characteristics are generally required in industry.

Figure 3 shows the relationship of rheological characteristics of PCWS (with different additives) with pH at solid concentration of 69 wt%. It can be seen that the PCWSs with NDF and MF additives were dilatant fluids and had shear-thickening properties at pH from 5 to 11 and exhibited the feeblest shear-thickening at pH of 9, while the PCWSs with LS and PS additives possessed shear-thinning pseudoplastic characteristics at pH of around 9.

A three-parameter Herschel–Bulkley model (Ma et al. 2013a, b) expressed by Eq. (1) was used to fit the shear stress–shear rate data.

$$\begin{cases} \dot{\gamma} = 0 & \tau \le \tau_y \\ \tau = \tau_y + k\dot{\gamma}^n & \tau > \tau_y \end{cases} \quad (1)$$

where $\dot{\gamma}$ is the shear rate, s^{-1}; τ is the shear stress, Pa; τ_y is the yield stress, Pa; k is the consistency coefficient, Pa s^n; n is the dimensionless flow characteristic exponent.

The parameter "n" can correctly reflect rheological characteristics of PCWS (Ma et al. 2013a, b). When $n > 1$, the PCWS is a dilatant fluid; otherwise, it is a pseudoplastic fluid. Furthermore, the smaller the value of n, the greater the pseudoplastic characteristics.

Figure 4 shows the relationship of flow characteristic exponents of the PCWSs with pH when the PCWSs were prepared with different additives at solid concentration of 69 wt%. It can be seen that the flow characteristic exponents all decreased first and then increased with increasing pH, and the smallest flow characteristic exponent with each additive appeared at pH of 9, indicating that pH of around 9 was the most favorable acid–alkali environment to strengthen pseudoplastic characteristics of PCWS.

This is because pH can affect interactions between the additive and particles and then affect the rheological characteristics of slurry. The alkaline additives can maintain their own activity and react sufficiently with surface of particles only in moderate alkaline environment, and make

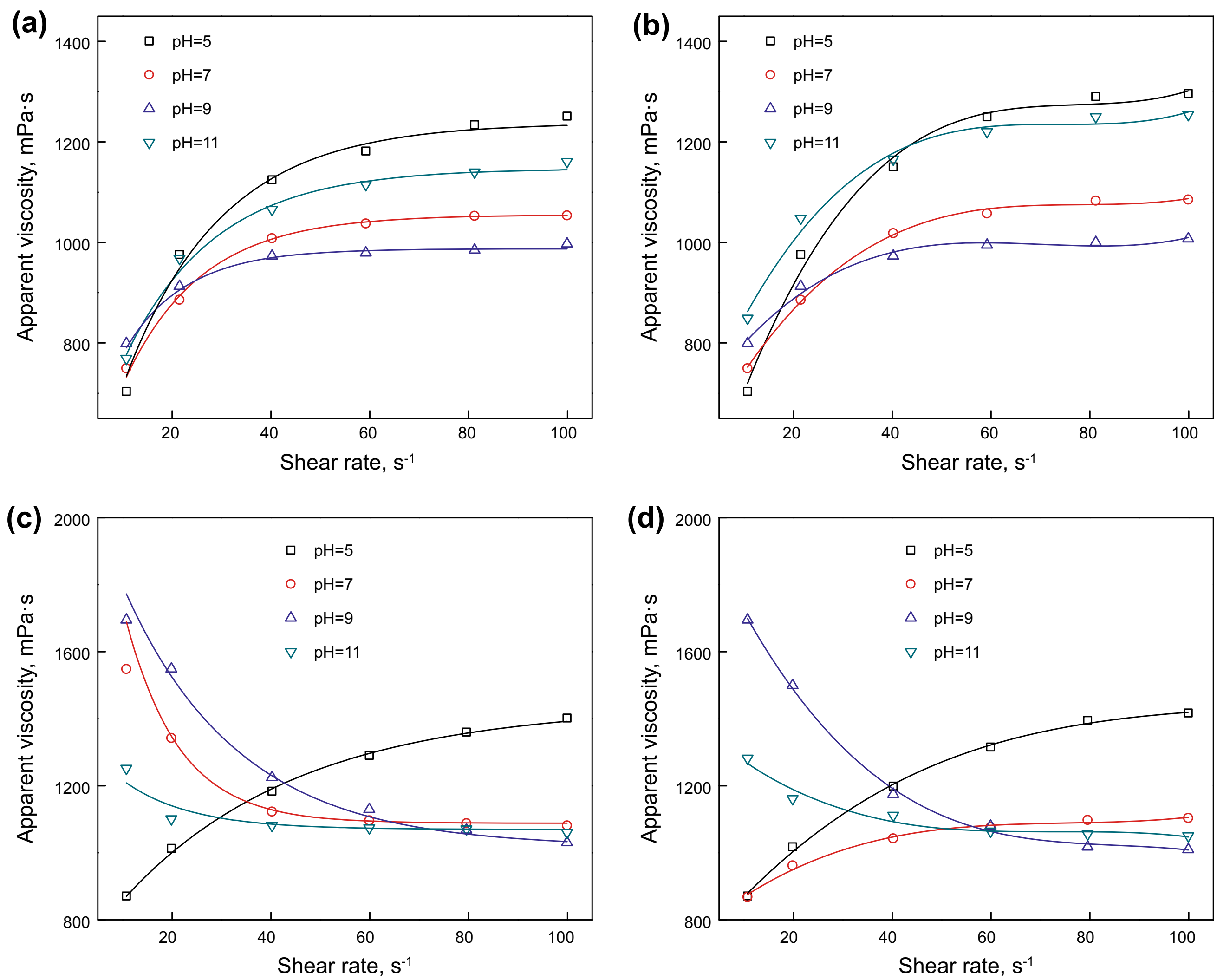

Fig. 3 Rheological characteristics of PCWS (with different additives) at different pH values. **a** PCWS with NDF, **b** PCWS with MF, **c** PCWS with LS, **d** PCWS with PS

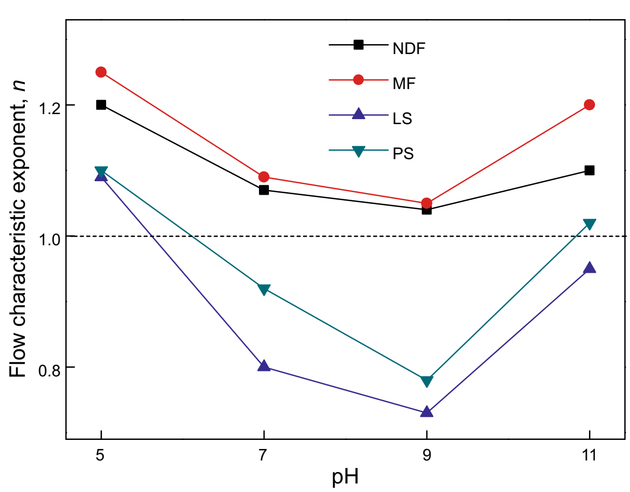

Fig. 4 Effects of pH on flow characteristic exponent

it possible to form a relatively stable three-dimensional network structure in slurry and present relatively strong pseudoplastic characteristics.

3.3 Effects of pH on stability of PCWS

Figure 5 shows the trends of stability indexes of the PCWSs with pH when the PCWSs were prepared with different additives at solid concentration of 67 wt%. It can be seen that both the relative height of hard sediment layer and the separated water rate decreased first and then increased with increasing pH, and the smallest relative height of hard sediment layer and the smallest separated water rate both appeared at a pH of 9. The PCWSs with LS or PS additives even did not produce hard sediment at pH of 9, as shown in Fig. 5a, indicating that a pH of around 9 was the most favorable acid–alkali environment to strengthen stability of PCWS.

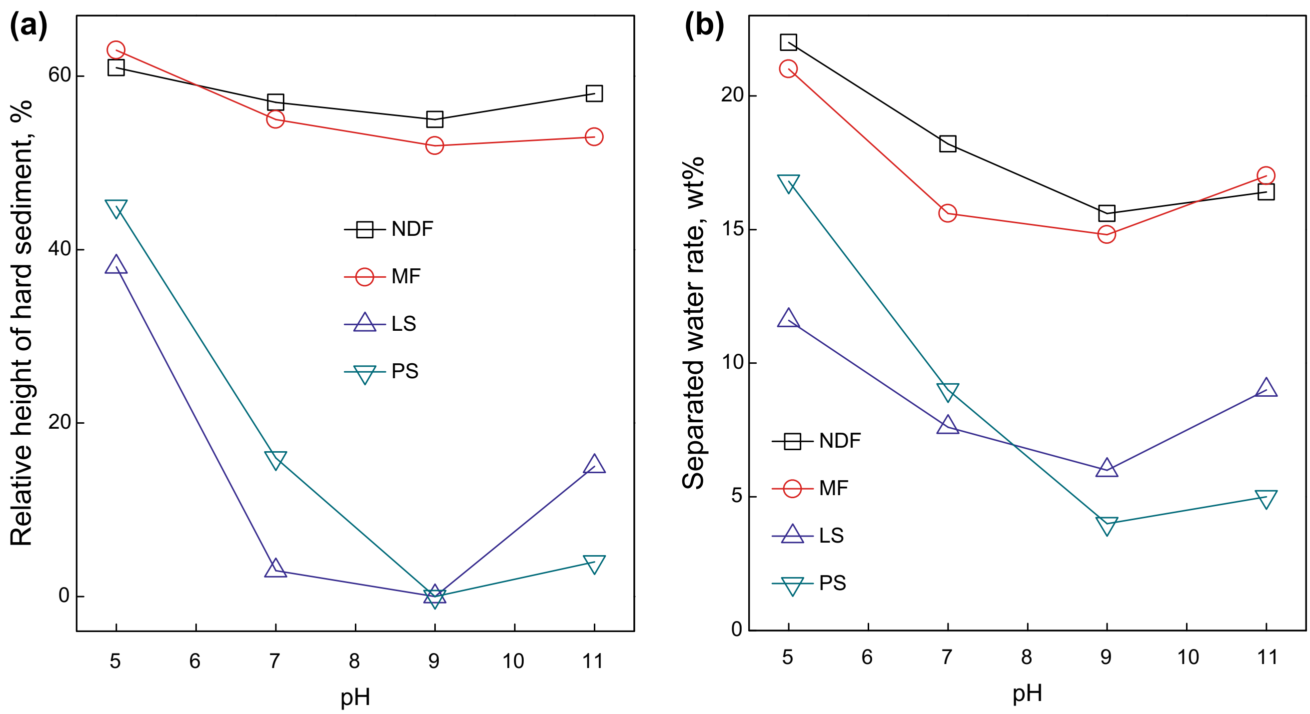

Fig. 5 Effects of pH on stability of PCWS by **a** rod-insertion method and **b** visual method

There is a positive correlation between stability and pseudoplastic characteristics of PCWS. The more stable the three-dimensional network structure of slurry is, the better the stability turns out to be. Therefore, a pH of around 9 can also be the best acid–alkali environment to obtain good stability of PCWS.

4 Conclusions

Through the study, the following conclusions can be drawn:

1. The slurrying concentration of the PCWS increased first and then decreased with increasing pH from 5 to 11. An acid environment was an unfavorable factor to the slurrying concentration. The optimal pH to obtain best slurrying concentration was 9. The additives used in this work themselves possess moderate alkalinity, and their activity can be restrained in acid or strong alkali conditions, leading to worse dispersion of particles and decreased slurrying concentration.
2. The pseudoplastic characteristics of the PCWS increased first and then decreased with increasing pH from 5 to 11, and a pH of around 9 was the most favorable acid–alkali environment to strengthen the pseudoplastic characteristics. The alkaline additives can maintain their own activity and react sufficiently with surface of particles only in a moderate alkaline environment, and make it possible to form a relatively stable three-dimensional network structure in slurry and present relatively strong pseudoplastic characteristics.
3. The stability of the PCWS increased first and then decreased with increasing pH from 5 to 11, and the best stability occurred when the pH was around 9. A pH of around 9 was the best acid–alkali environment to obtain good stability of PCWS. It shows a positive correlation between stability and pseudoplastic characteristics of PCWS.

Acknowledgments The authors would like to acknowledge the financial support from the National Natural Science Foundation of China (No. 51506185) and the Zhejiang Provincial Natural Science Foundation of China (No. LQ15E060002).

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