Sugarcane bagasse for environmentally friendly super-absorbent polymer: synthesis methods and potential applications in oil industry

Shabrina Sri Riswati*, Rini Setiati, Sugiatmo Kasmungin, Suryo Prakoso, and Muhammad Taufiq Fathaddin

Department of Earth and Energy Technology, Trisakti University, Jakarta, Indonesia

*shabrina@trisakti.ac.id

Abstract. Super-absorbent polymer (SAP) is able to absorb water by multiple times more than its own weight. Sugarcane bagasse (SCB) raw material has been excessively produced as a by-product in sugar factory. The synthesis of SAP from SCB creates a balance between the utilization of industrial by-product and the resulted environmentally friendly material. In oil production water might be a troublesome, thus minimizing water production while extracting oil is essential. Besides, diversion of the flow in heterogeneous reservoir optimizes the oil production. SCB-SAP might have the potential to act as a water absorbing agent and flow diverter by taking the advantage of SAP high swelling ratio characteristic. This study provides the information of SCB-SAP synthesis methods and highlights the current application of SAP in oil industry, including the laboratory studies and field tests.

1. Introduction

Super-absorbent polymer (SAP) started becoming attractive in 1950s due to the massive use in the sanitary industry [1]. Chemical or physical bonding builds cross-linking between long macromolecular chains. The bonding results in the creation of polymer network which later be called as superabsorbent [2]. SAP is a hydrophilic material that swells in aqueous solution and retains the water in its structure [3]. The absorption capacity of SAP is larger than the common hydrogels, i.e., 500-1500 g/g compare to 1000 g/g for common hydrogels [3-5].

Sugarcane bagasse (SCB) is a great source of cellulose coming from the agro-industrial by-product of the sugar and alcohol industries. The utilization of SCB is normally limited for paper manufacture and as a fuel in sugar factory. SCB can be categorized as a renewable resources with relatively short re-production cycle [6]. The extraction of cellulose as the raw material of SAP synthesis allows SCB to become a suitable candidate for making environmentally friendly SAP compare to the commercial synthetic ones [1-3].

The cellulose-based SAP have been proven to be able functioning in agriculture and horticulture, personal health care, water treatments, and biomedical [1]. In the oil industry, SAP is usually termed as preformed particle gel (PPG) [7 and 10]. It is used as a flow diverter in heterogeneous reservoir for the conformance control and an oil displacement agent [7-10]. In common, synthetic SAPs are employed assisting the oil production. Therefore, the study on the potential use of the organic SAP, particularly
SCB-SAP in oil industry is wide open. The objective of this study is to provide information on the synthesis methods of SCB-SAP and current applications of SAP in oil industry. This study may also serve an insight for future development and potential utilization of SCB-SAP.

2. The SCB raw materials

The extraction of sugar from the sugarcane results in fibrous by-product called SCB. The schematic of the sugar extraction process is drawn in Figure 1. SCB is one of the most important by-product, where a large number of SCB is produced every year, i.e., 54 million dry tons throughout the world [11]. Heat and power generation to drive the sugar milling required half of the total produced SCB and the other half is stored. The economic value of the stored SCB is low. The stored SCB may also cause environmental problem to the sugar factory and neighboring area [12].

About 50% of SCB consists of cellulose, while the rest are hemicellulose and lignin with the same proportions [13]. The cellulose has two structures, i.e., crystalline and amorphous structures that are bound together by the hydrogen bonding. Lignin contributes the structural support, impermeability, oxidative stress resistance, and microbial attack protection towards SCB. The cellulose and lignin are connected by the hemicellulose, which gives the rigidity towards cellulose-hemicellulose-lignin network [2].

The crystal and ordered structures are the reason behind the reaction problem between cellulose and other substances [14]. Thus, native cellulose has to undergo pretreatment to disturb the crystalline structure and break the lignin support. The pretreatment can be performed through thermal pretreatment, comminution, steam pretreatment/steam explosion, acid pretreatment, alkaline pretreatment, oxidative pretreatment, ammonia pretreatment, carbon dioxide pretreatment and their combination [6]. Mechanical activation (MA) accentuates mechanical activity to modify the structure of cellulose, e.g., friction, collision, impingement, or shear [6].
3. Synthesis method and characterization analysis of SCB-SAP

In general, the synthesis method of SAP can be differentiated into two ways: chemical and physical methods. The cellulose-based SAPs are mainly synthesized by the formation of covalent bond from the chemical method. Meanwhile, the physical methods forms hydrogen or ionic bond between polymers to build molecular crosslink [1]. The synthesis methods that have been used by several researchers to fabricate the SCB-SAP can be classified into graft copolymerization [2 and 6], free radical graft copolymerization [12], extrusion method [15], and electron beam irradiation [16]. The specific name of SCB-SAP and its synthesis methods are summarized in Table 1. Graft copolymerization is the other term of graft polymer since minimum two different monomers are grafted. It optimizes the properties of the polymer by grafting monomer molecules into it. In graft polymerization, initiators are required in the process. Ammonium persulfate (APS) and sodium sulfite (SS) are used as the initiators, and anhydrous methanol removes the unreacted monomer [6]. Liang [2] added N,N-methylenebisacrylamide (MBAAm) as the cross-linking agent.

Free radical graft copolymerization uses oxygen-free nitrogen gas to facilitate radical formation, N,N'-methylene-bis-acrylamide (MBA) as the crosslinker, and APS for the initiator [12]. In the extrusion method, polymer and chemical reacts in a single continuous process by the use of extruder [15]. In addition, the radicals will also form by applying radiation into the aqueous polymer solution, which then recombine on different chains and results in covalent bond. Polyacrylamide (PAM) is mixed with the cellulose from the SCB before applying electron beam irradiation. The separation of unreacted polymer is done by using centrifuge [16].

Characterizations that are commonly carried out for SCB-SAP are swelling measurement, grafting ratio and efficiency calculation, chemical structure and morphology studies. Huang [6] found out that mechanical activation promoted the graft copolymerization by analyzing grafting ratio and grafting efficiency. The granular morphology, crystal structure, functional group, and thermal properties are examined by the scanning electron microscopy (SEM), X-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR), and differential scanning calorimetry (DSC), respectively. Ren [12] confirmed excellent water retention capacity and copper (II) adsorption of SCB-SAP. Neamjan [15] concluded that the SCB-SAP improves the soil moisture retention, hence it potentially be used as an agricultural water resource.

Table 1. SCB-based SAP synthesis method.

| SAP                                      | Synthesis method                      |
|------------------------------------------|---------------------------------------|
| SCB-superabsorbent hydrogels (SAH)      | Graft copolymerization                |
| SCB-biodegradable SAH                    | Graft copolymerization                |
| Sugarcane bagasse-g-poly(acrylic acid-co-acrylamide) (SB/P(AA-co-AM)) hydrogels | Free radical graft copolymerization |
| Biodegradable SCB-SAP                    | Extrusion method                      |
| SCB-SAP                                  | Electron beam irradiation             |

4. Application of SAP in oil industry

Muhammed [7] proposed hybrid technique of PPG and surfactant to create a synergy between enhancing oil recovery and minimizing water production in heterogeneous mature reservoirs. Their preliminary study showed that the injectivity of PPG was improved by surfactant without affecting the plugging efficiency. Yousufi [17] suggested that the unique properties of a hybrid nano-composite hydrogel, Carboxylated Multi-Walled Carbon Nanotubes (CMWCNTs) contained SAP, i.e., the swelling capability, stability in low pH, and moderate absorption capacity at high temperature, support the potential application in Enhanced Oil Recovery (EOR). Zhao [8] concluded that dispersed particle gel strengthened polymer-surfactant (DPS) system as an EOR agent for high water cut mature oilfields was superior to the Polymer Surfactant (PS) flooding due to the synergistic effects of the swept volume.
capacity and high displacement efficiency. A micron-size polyacrylamide elastic microsphere (MPEM) was suitable for controlling microscopic profile and displacing oil in heterogeneous reservoir [18]. The mandatory characteristics of a chemical that is used for water control treatment purpose are high salinity and hardness tolerance, water ion content compatibility, thermal stability, low viscosity, excellent suspension dispersibility, insensitive to shear, and having deep penetration [19].

The technology of micro-gel, SAP with micron size, flooding has been applied for trial in worldwide oilfield [8]. In Chinese oilfields, PPG has been successfully applied in water flooding, polymer flooding, and ASP flooding. It contributed to the increase of oil production rate and the decrease of water production through conformance control mechanism [20]. Bai [10] showed that the field tests of particled superabsorbent cross-linking polymer or PPG in Zhongyuan and Daqing oilfield, China, effectively corrects the permeability heterogeneity of the reservoirs with fractures or channels. The problem of short circuiting in Al Shaheen reservoir, offshore Qatar, could be solved by employing crystalline superabsorbent copolymer for conformance [9]. Yao [19] highlighted the importance of matching factor between the particle size of pore-elastic microspheres and pore throat to assess the profile control and oil displacement. They also reported a success field application of elastic microspheres in Block Liu 28-1, Jidong oilfield, China. Table 2 summarized the current application of SAP in oil industry.

### Table 2. SAP application in oil industry.

| SAP                        | Study scale | Function of SAP                                                                 |
|----------------------------|-------------|---------------------------------------------------------------------------------|
| Preformed particle gel (PPG) | v           | EOR agent, minimizing water production in heterogeneous mature reservoirs, and correcting permeability heterogeneity |
| Carboxylated Multi-Walled Carbon Nanotubes (CMWCNTs) contained SAP | v           | EOR agent                                                                       |
| Dispersed particle gel strengthened polymer-surfactant (DPS) | v           | EOR agent for high water cut mature oilfields                                   |
| Micron-size polyacrylamide elastic microsphere (MPEM) | v           | Microscopic profile control and oil displacement agent                          |
| Micro-gel                  | v           | EOR agent                                                                       |
| Crystalline superabsorbent copolymer | v           | Conformance treatment of waterflooded horizontal well                            |
| Pore-elastic microspheres  | v           | Profile control and oil displacement agent                                        |

5. **Outlook**

This study focuses on the current status of SCB-SAP synthesis and SAP application in oil industry. As an organic material, SCB-SAP is equipped with favorable properties of hydrophilic, biodegradable, biocompatible, transparent, and non-toxic. Besides, SCB-SAP is resistant to salinity, temperature, and pH, hence it is suitable for the production improvement agent in the oil reservoirs with high variation of reservoir conditions. In most of the cases, synthetic SAPs are employed in oil production process. For that, future study could be devoted to develop the fabrication of organic SAP, particularly from SCB due to the resource-abundant and examine the potential of SCB-SAP application in oil industry. A positive synergy can be achieved from using a low-cost environmentally friendly material to improve the oil recovery.
References

[1] Ma, J., Li, X. and Bao, Y., 2015. Advances in cellulose-based superabsorbent hydrogels. RSC advances, 5(73), pp.59745-59757. https://doi.org/10.1039/C5RA08522E

[2] Liang, X., Huang, Z., Zhang, Y., Hu, H. and Liu, Z., 2013. Synthesis and properties of novel superabsorbent hydrogels with mechanically activated sugarcane bagasse and acrylic acid. Polymer bulletin, 70(6), pp.1781-1794. https://doi.org/10.1007/s00289-013-0921-4

[3] Ma, X. and Wen, G., 2020. Development history and synthesis of super-absorbent polymers: a review. Journal of Polymer Research, 27, pp.1-12. https://doi.org/10.1007/s10965-020-02097-2

[4] Fang, L., Zhao, Y. and Tan, T.W., 2006. Preparation and water absorbent behavior of superabsorbent polyaspartic acid resin. Journal of polymer Research, 13(2), pp.145-152. https://doi.org/10.1007/s10965-005-9022-x

[5] Zhang, Y., Wang, L., Li, X. and He, P., 2011. Salt-resistant superabsorbs from inverse-suspension polymerization of PEG methacrylate, acryamide and partially neutralized acrylic acid. Journal of polymer research, 18(2), pp.157-161. https://doi.org/10.1007/s10965-010-9402-8

[6] Huang, Z., Liang, X., Hu, H., Gao, L., Chen, Y. and Tong, Z., 2009. Influence of mechanical activation on the graft copolymerization of sugarcane bagasse and acrylic acid. Polymer Degradation and Stability, 94(10), pp.1737-1745. https://doi.org/10.1016/j.polymdegradstab.2009.06.023

[7] Muhammed, F.A., Bai, B. and Tang, T., 2012. Experimental study of the interaction between surfactants and super absorbent polymer gel. Journal of Petroleum Science and Engineering, 90, pp.159-164. https://doi.org/10.1016/j.petrol.2012.04.010

[8] Zhao, G., Li, J., Gu, C., Li, L., Sun, Y. and Dai, C., 2018. Dispersed particle gel-strengthened polymer/surfactant as a novel combination flooding system for enhanced oil recovery. Energy & Fuels, 32(11), pp.11317-11327. https://doi.org/10.1021/ac502720

[9] Pedersen, M.H., Ritchie, B., Pon, Z.A., Brink, D.I., Abbasy, I. and Jaafar, M.R., 2009, January. Case study: Successful application of a novel conformance treatment in an extended reach horizontal well in the Al Shaheen field, offshore Qatar. In Offshore Europe. Society of Petroleum Engineers. https://doi.org/10.2118/123949-MS

[10] Bai, B., Li, L., Liu, Y., Liu, H., Wang, Z. and You, C., 2007. Preformed particle gel for conformance control: factors affecting its properties and applications. SPE Reservoir Evaluation & Engineering, 10(04), pp.415-422. https://doi.org/10.2118/89389-PA

[11] Ren, J.L., Geng, Z.C., Liu, C.F., Xu, F., Sun, J.X. and Sun, R.C., 2006. Fractional isolation and structural characterisation of hemicellulosic polymers from delignified and ultrasonic irradiated sugarcane bagasse. E-polymers, 6(1). https://doi.org/10.1515/epoly.2006.6.1.855

[12] Andriyanti, W., Suyanti, S. and Ngasifudin, N., 2012. Pembuatan dan karakterisasi polimer superabsorben dari ampas tebu. Prosiding Pertemuan dan Presentasi Ilmiah Teknologi
Akselerator dan Aplikasinya, 13, pp.1-7. ISSN: 1411-1349.

[17] Yousufi, M.M. and Hashmi, S., 2016. Carbon Nanotubes laced Superabsorbent Polymer for Enhanced Oil Recovery Technology. Advanced Materials and Process Engineering Conference, Karachi, Pakistan, 1, p.268.

[18] Yao, C., Lei, G., Hou, J., Xu, X., Wang, D. and Steenhuis, T.S., 2015. Enhanced oil recovery using micron-size polyacrylamide elastic microspheres: underlying mechanisms and displacement experiments. Industrial & Engineering Chemistry Research, 54(43), pp.10925-10934. https://doi.org/10.1021/acs.iecr.5b02717

[19] Yao, C., Lei, G., Li, L. and Gao, X., 2012. Selectivity of pore-scale elastic microspheres as a novel profile control and oil displacement agent. Energy & fuels, 26(8), pp.5092-5101. https://doi.org/10.1021/ef300689c

[20] Qiu, Y., Wu, F., Wei, M., Kang, W. and Li, B., 2014, April. Lessons learned from applying particle gels in mature oilfields. In SPE Improved Oil Recovery Symposium. Society of Petroleum Engineers. https://doi.org/10.2118/169161-MS