Journal of Natural Gas Science and Engineering 32 (2016) 491–500

Contents lists available at ScienceDirect

Journal of Natural Gas Science and Engineering

journal homepage: www.elsevier.com/locate/jngse

Hydraulic fracture fluid for gas reservoirs in petroleum engineering applications using sodium carboxy methyl cellulose as gelling agent

Abdulmumin O. Aliu, Jianchun Guo, Shibin Wang*, Xing Zhao

State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu, China

ARTICLE INFO

Article history:
Received 12 January 2016
Received in revised form
1 March 2016
Accepted 21 March 2016
Available online 24 March 2016

Keywords:
Crosslinking
Stabilizer
Cellulose
Sodium carboxy methyl cellulose
Breaker

ABSTRACT

In this present work, a cellulosic based hydraulic fracturing fluid was prepared for gas reservoirs, using sodium-carboxy methyl cellulose (Na-CMC) as gelling agent which is to be applied in petroleum engineering field. The prepared Na-CMC hydraulic fracturing fluid for gas reservoirs was tested for basic rheological performances. Viscosity of the linear and crosslinked forms of the fluid were measured at elevated temperature of about 90 °C and at shear rate of 170/s. The network structure of the Na-CMC fracture fluid was analyzed using scanning electron microscope (SEM). During SEM image test, different forms of the Na-CMC aqueous mixtures were tested such as linear, crosslinked and stabilized-crosslinked forms. Sodium thiosulfate was used as gel stabilizer at elevated temperature and shear rate. Breaking/Residue tests were also carried out to see how much of residue will be left after breaking the fluid using a sodium and ammonium salt of persulfate as gel breaker.

Results showed that Na-CMC fluid was able to maintain an excellent viscosity at temperate of 90 °C when compared to guar which is the most used gelling agent in area of hydraulic fracturing treatments. Although SEM results showed that Na-CMC's physical network structures were very connected in its linear form which gave a bit lower viscosity compared to when Carboxy methyl hydroxy ethyl cellulose (CMHEC) was used for gelling.

The SEM images of Na-CMC further showed a highly aggregated network structure after crosslinking and even more aggregation after addition of the gel stabilizer of 0.3 wt%. Hydro propyl guar (HPG) and Na-CMC were adopted for breaking test using sodium persulfate (SP) and ammonium persulfate (AP) at 0.3wt% for 17 h under a temperature of 65 °C. Less residue were found in Na-CMC when compared to HPG powder which is commonly used in the industry as gelling agent today. This less residue formed will yield good fracture conductivity for the proppant pack and fracture network.

1. Introduction

Carboxy methyl cellulose is a derivative of cellulose which is usually manufactured in its sodium salt form to give sodium carboxy methyl cellulose. it comes as a white or milky powder and it is typically ionic, odorless and tasteless derivative. The molecular formula of Na-CMC is $C_6H_7O_2(OH)_2OCH_2COONa$, when its degree of substitution (DS) is 1. DS is the number of hydroxyl group substituted per anhydrous glucose monomer. The DS of CMC affects its solubility to a great extent. A DS of 0.3 indicates alkaline solubility while DS of above 0.4 indicates water solubility. However CMC is often not soluble in organic solvent like methanol, acetone, chloroform or benzene. The CMC solution transparency improves with increase in its DS. The schematic, illustrating the chemical structure of Na-CMC is shown in Fig. 1.

In this current work, Na-CMC is to be applied as gelling agent in hydraulic fracturing fluid preparation. Hydraulic fracturing is a very common procedure used to stimulate reservoir rock, in order to optimize production. Hydraulic fracturing involves injecting high viscous gel or low viscosity slick water at high flow rate, so as to create fracture network in the reservoir rock. The injected fracturing fluid into gas reservoir must have the ability to transport proppants down to the fracture tip in order them opened. After pumping is ceased, the proppants remain within the fracture network, thereby keeping the fracture opened (Trabelsi and Kakadjian, 2013). Guar and its derivatives the most used gelling agents for hydraulic fracturing fluid preparation in petroleum industry for hydraulic fracturing treatment (Legemah et al., 2013).

* Corresponding author.
E-mail address: wangshb07@163.com (S. Wang).

http://dx.doi.org/10.1016/j.jngse.2016.03.064

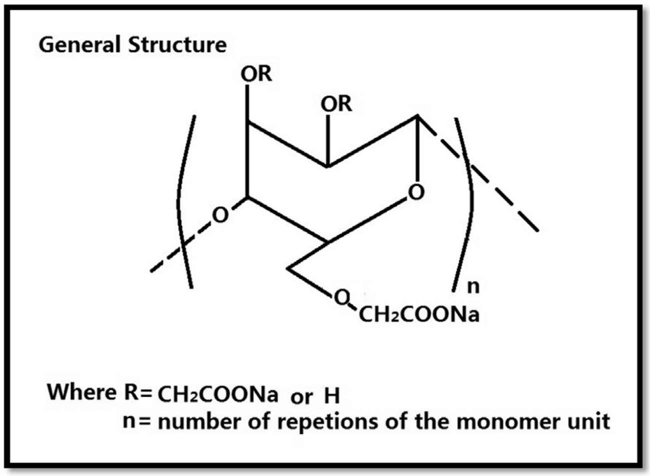

Fig. 1. Schematic of Chemical structure of Sodium-CMC.

However, there are draw backs experienced in the use of guar and its derivatives. These include cost factor and high residue left behind after breaking the fluid to lower viscosity, leading to damage or poor fracture conductivity of the proppant pack and fracture network. Therefore, Na-CMC was adopted to solve these problems faced by guar. Majority of fracture treatments adopt the use of visco-elastic fluid (VEF) so as to be able to transport these proppants effectively and also be able to withstand high shear in the process (Harris et al., 2008). Elastic property of the fluid is an important parameter of the VEF and their ability to transport proppants (Harris et al., 2005; Naval et al., 2001). Therefore all hydraulic fracturing fluids should posses such rheological properties. This is another reason why we have decided Na-CMC be adopted as gelling agent in hydraulic fracturing fluid, due to its ability to give high viscosity at low concentration (Yang and Zhu, 2007).

In terms of current market cost price, Na-CMC is cheaper and less expensive than guar. Na-CMC or cellulose gum as it is popularly called, costs about USD 2400–2500/metric ton (Alibaba, 2016a) while HPG or guar gum, costs USD3000-3200/metric ton (Alibaba, 2016b). Therefore Na-CMC seem to be more economical to be adopted as gelling agent.

Various literatures have reported some progress about the behavior of Na-CMC in solution. The effect of temperature and concentration on apparent viscosity of aqueous Na-CMC solution was modeled over power law range (Cheng-Xian and Shao-Yen, 1995). Based on Newtonian theory, effect of shear induced recombination of CMC macromolecular crystallites was proposed (Jayabalan, 1989). Rheological behavior of CMC and Xanthan mixture was studied under a non destructive shear condition (Florjancic et al., 2002).

In 1999, it was proven by Mothe and Rao, that the viscosity of Na-CMC exponentially increases with its concentration. It was also stated that a lot of polymer solution, has the tendency of been described by the Huggins and Kramer equation (Mothe and Rao, 1999).

Most previous research work done focused on linear form of the Na-CMC, but this work focused on crosslinked form of the Na-CMC, which makes this research work a more challenging task. Some giant oil service companies have done some extensive research in this area, but very little facts about this area are made available to these giant companies because of the technology involved is still a little new and highly researched upon.

CMC has a broad range of application, some of which are as follows; Based on spectacular viscosity properties of CMC, its reaction with mucin and its reaction with 5-fluorouracil gave a unique result useful in manufacturing anti-cancer drugs (Rossi et al., 1996) (Nishida et al., 1982). CMC was studied to understand the poly-electrolyte effect in CMC water-cardoxene solution using translational diffusion and viscometry (Okatova et al., 1990). Investigation was carried out, to study the effect of polyion charge on specific viscosity of CMC (Trivedi and Patel, 1987). Viscosity response of multivalent metal ion-containing CMC was also researched (Heinze et al., 1994). The preparation and characterization of konjac glucomannan and Na-CMC blend films was also studied (Xiao et al., 2001).

Based on this current work, tetra-triethanolamine zirconate, a unique complex was adopted in the crosslinking Na-CMC. The valency or coordination number of Zirconium (Zr) is +4, therefore, Zr can form a very strong covalent bond as shown in Fig. 2. The bonding of the Zr ion to Na-CMC chemical structure is temperature and pH dependent. Due to the strong convent bonding, the zirconium crosslinked Na-CMC gel can withstand high shear rate. Most times, crosslinking using zirconium compound is advised to be delayed to 2/3 of pipe time, due to its fast crosslinking action. The zirconium based crosslinker has a unique property of stabilizing at broad range of pH (Montgomery, 2013).

2. Materials and methods

2.1. Preparation/procedure

Experiments were done at laboratory scale to simulate the field scale. All analysis done was for us to have idea of how Na-CMC crosslinked gels behave rheologically. Results obtained is not precise for field standards but just for analysis and comparison.

2.1.1. Preparing hydrated solution of Na-CMC

In preparing sodium-CMC hydrated fracturing fluid, a commercially available derivative of cellulose called sodium carboxy methyl cellulose ($C_6H_7O_2(OH)_2OCH_2COONa$) powder was obtained from a qualified supplier for the purpose of this

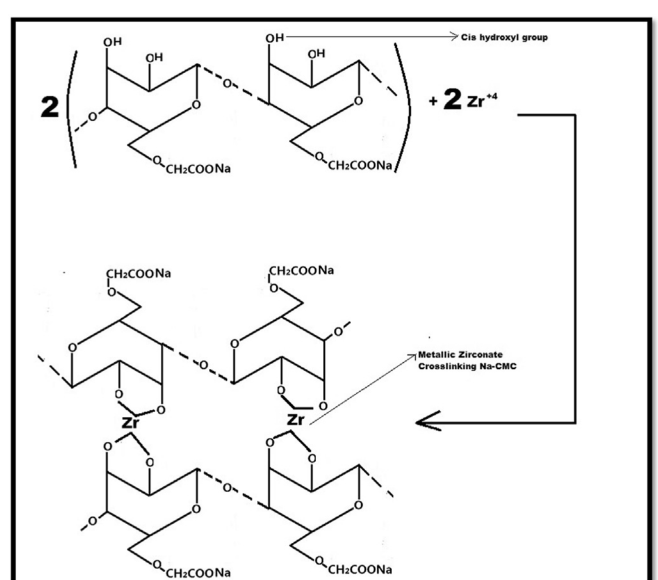

Fig. 2. Schematic of Zirconium metallic crosslinker, bonding on Na-CMC.