Industrial Crops and Products 93 (2016) 152–160

Contents lists available at ScienceDirect

Industrial Crops and Products

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

Sandstone injectivity and salt stability of cellulose nanocrystals (CNC) dispersions—Premises for use of CNC in enhanced oil recovery

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ARTICLE INFO

Article history:
Received 30 October 2015
Received in revised form 19 February 2016
Accepted 9 March 2016
Available online 5 April 2016

Keywords:
Oil recovery
Nanocellulose
CNC
Injectivity
Salt stability

ABSTRACT

Reservoir production is frequently supported by using flooding fluids, often seawater. The efficiency is affected by various factors, such as the wettability of the reservoir rock and the mobility ratio between reservoir oil and injected fluid phase. These factors again influence sweep efficiency, which is the fraction of the total reservoir oil volume in contact with injected fluid during oil recovery. Addition of nanoparticles can affect the sweep efficiency on a macroscopic level by increasing the volume of petroleum in contact with the flooding fluid. Presented here are core-flooding studies performed using cellulose nanocrystals (CNC) of different concentrations in low-saline water. The studies were performed to investigate the injectivity of CNC into a high-permeable sandstone core, and to observe the effects addition of electrolytes had on the rheological properties of a low concentration dispersion of CNC. Zeta- potential and shear viscosity of dilute dispersions containing CNC was investigated under increasing electrolyte concentration. The flooding experiments show that the CNC has good injectivity in sandstone for all concentrations used, and the viscosity measurements performed on the effluent prove that the particles are able to travel through the core. Being sufficiently small for injection into sandstone and showing good colloidal stability at low salinities, CNC particles have the premises necessary to function properly as a flooding additive for enhanced oil recovery (EOR) in sandstone reservoirs.

1. Introduction

Oil reservoirs worldwide will contain nearly 2×10^{12} barrels (0.3×10^{12} m^3) of conventional oil and 5×10^{12} barrels (0.8×10^{12} m^3) of heavy oil after conventional oil recovery has been performed (Thomas, 2008). Although the percentage of remaining oil will vary from field to field, a study investigating 10 US oil producing areas found that around two thirds of original oil in place (OOIP) remained when traditional recovery methods were exhausted (U.S. Department of Energy (DOE), 2006). According to the Norwegian Åm Report (2010), an increase in oil recovery of 1% from the Norwegian shelf is worth 270 billion NOK, or almost 34 billion USD (Åm et al., 2010).

Oil recovery is usually categorized into three different phases/sections, and although there are some discussions regarding this (Al-Mjeni et al., 2010), these are roughly primary, secondary and tertiary oil recovery. Primary oil recovery is production of oil from a reservoir using only natural energy that is present in the reservoir, e.g. by reducing the pressure in the well (Ahmed, 2010). Main driving forces in primary recovery can for example be natural water-drive, fluid expansion, rock compaction and gravity drainage (Green, 1998). Natural driving forces are unfortunately not very efficient and will result in an overall low oil recovery. Secondary oil recovery utilizes injection of water or gas to maintain reservoir pressure and to displace the oil towards the producing well (s) (Ahmed, 2010; Green, 1998). The last phase of recovery is called tertiary or enhanced oil recovery (EOR). It is shortly defined as: "Methods aimed at increasing ultimate oil recovery by injecting appropriate agents not normally present in the reservoir, such as chemicals, solvents, oxidizers and heat carriers in order to induce new mechanisms for displacing oil" (Bavière, 1991).

The term "EOR" must not be confused with "IOR" (improved oil recovery), although they have been used interchangeably and non-consistently throughout the years. IOR is a general term meaning improving oil recovery in any possible way, while EOR is more specific, focusing on "a reduction in oil saturation below the residual oil saturation (S_{or})" (Thomas, 2008). S_{or} is defined as the amount of oil trapped in pore spaces. This effect is due to high surface

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http://dx.doi.org/10.1016/j.indcrop.2016.03.019
0926-6690/

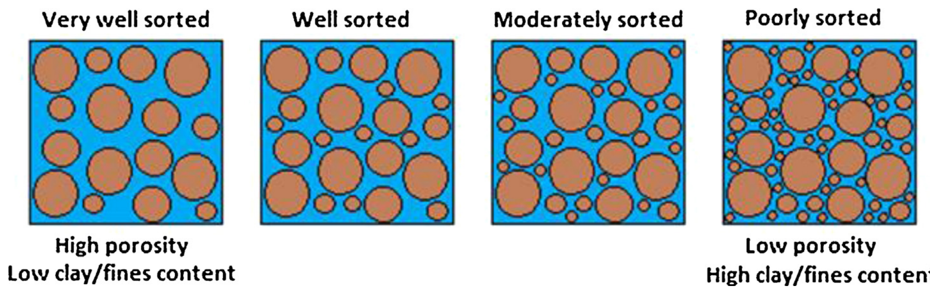

Fig. 1. Reservoir quality is dependent on the sorting and packing of grains, as well as clay and fines content.

tension at the oil-water interface, where the water will attempt to displace the oil out of the pores through very small capillaries, leading to a discontinuous oil phase. The oil droplets are "snapped" off, or capillary trapped, and are thus held back in the pores (Jahn et al., 2008b). All EOR methods have a main goal of increasing the volumetric (macroscopic) sweep efficiency and enhancing the displacement (microscopic) efficiency. The volumetric sweep is increased by reducing the mobility ratio between the displacing and the displaced fluid. The microscopic entrapment could be lowered when the interfacial tension (IFT) between the displacing and displaced fluids is reduced. This gives a lower S_{or} and thus a higher ultimate oil recovery (Zolotukhin and Ursin, 2000a).

In this paper, the focus will be on chemical EOR (non-thermal EOR), as in polymer flooding, where a suitable polymer is added to the injection water. Polymer flooding is usually applied in reservoirs containing high-viscosity oil, or in heterogeneous reservoirs, where the oil-bearing layers are of different permeabilities (Zolotukhin and Ursin, 2000b). The main goals when using polymers for EOR is thus to improve the mobility ratio and reduce the effective permeability of the displacing fluid in highly permeable zones (Latil, 1980; Littmann, 1988). Today, in most cases, there are two types of water-soluble polymers in use; synthetic polyacrylamides (PAMs) and xanthan, which is a biopolymer (polysaccharide). Most polymer floods are driven by very dilute brine (less than 10.000 ppm total dissolved solids) (Chang, 1978; Thomas, 2008).

Sandstone is a clastic rock which is formed through transport and deposition of mechanically and chemically weathered material. It consists mainly of quartz (SiO_2), which is one of the most stable minerals, and variable amounts of feldspars and clay. Reservoir quality depends on the sorting of these sediments, as well as the quantity and distribution of clay. Clay content can have a large impact on the permeability and porosity of sandstone. High clay content, combined with a mixture of poorly sorted particles will give a low porosity and low hydrocarbon storage capacity, while well sorted particles yields high porosity and thus good capacity for storing hydrocarbons (Jahn et al., 2008a), as shown in Fig. 1.

A high quality reservoir typically has pore sizes larger than 30 μm (macropores), and pore throats with diameters larger than 10 μm. At the other end of the scale, low quality conventional reservoir rock has "microporosity", with pore sizes below 10 μm and pore throats smaller than 1 μm. Below this, the sediment is regarded as a gas-tight sandstone, and is more likely to have a cap function (Nelson, 2009). A typical outcrop sandstone core used for flooding experiments is shown in Fig. 2.

Cellulose nanocrystals (CNC) is a potential new bio-based flooding material. It is a natural polysaccharide derived from various cellulosic sources, the most common ones being wood and cotton (Dufresne, 2013; Hamad, 2006; Klemm et al., 2011). CNC was first described by Rånby in 1949 (Ranby, 1949), and is defined as crystalline, rod-like particles with sizes in the nanometer range. CNC is derived from cellulosic fibers, which are semi- crystalline, meaning they consist of both crystalline and amorphous regions. Through a hydrolysis reaction using mineral acids, the amorphous regions are removed, leaving only the crystalline regions. First, the chemical process removes hemicelluloses from the surface of the fiber, before the acid attacks the amorphous and thus easier available regions. The result is crystalline cellulose sections that are rod-like in appearance. The reaction is terminated by diluting the acid, and residual components are removed by repeated centrifugation and extensive dialysis. Sonication is usually applied afterwards to disperse the CNC into a stable dispersion. Parameters like the type of acid, acid concentration, hydrolysis temperature and time, and intensity of the sonication strongly affects the structure, chemistry and phase separation properties of the finished CNC dispersion (Beck-Candanedo et al., 2005; Bondeson et al., 2006; Dong et al., 1996; Marchessault et al., 1961).

Fig. 2. Outcrop sandstone core used in the flooding experiment.

Depending on the original source, the resulting crystallites vary in size, with diameters ranging from 5 to 70 nm and lengths from 100 to 250 nm from plant celluloses (Klemm et al., 2011). It is therefore plausible that CNC from wood will be injectable into sandstone, as even what is regarded a low quality reservoir will have pore sizes and pore throats larger than the dimensions of the crystallites (<10 μm and <1 μm, respectively). They are also shear resistant, comparable to HPAM, which has a tendency towards shear degradation (Gao, 2013; Nelson, 2009).

The surface properties of the cellulose nanocrystals are dependent on the type of mineral acid which is employed for the