Surfactant Phase Equilibria and Separation of Amphiphilic Extractives from Black Liquor in Kraft Cooking of Wood

Esa Pirttinen
Laboratory of Forest Products Chemistry, Helsinki University of Technology, Espoo, Finland

Per Stenius
Laboratory of Forest Products Chemistry, Helsinki University of Technology, Espoo, Finland and Ugelstad Laboratory, Norwegian University of Science and Technology, Trondheim, Norway

Kari Kovasin
SciTech Services Ltd, Rauma, Finland

INTRODUCTION

"Wood extractives" is a more or less operationally defined group of mainly low-molecular weight substances in wood, soluble either in organic solvents or water. The composition of these extractives, which in Nordic wood species constitute 2–7% of the wood dry solids, varies widely from species to species. "Resin" often is used as a collective name for lipophilic extractives (with the exception of phenolic substances) that are soluble in nonpolar organic solvents but insoluble in water. The main components of hardwood resin are sterols, fatty acids, fatty acid esters, alkanols, and some alkaines; in addition to these groups of compounds softwood resin also contain dicyclic and tricyclic resin acids.1,2

Solubilization and phase equilibria of low molecular weight amphiphilic and insoluble wood components (sodium abietate, sodium oleate, sterols, alkanols, fatty acids) modeling those occurring in the Kraft cooking process of papermaking pulps ("extractives") were investigated. The rate of separation (creaming) of particles formed when adding neutral solubilizes in excess to solutions of fatty and resin acids soaps was studied using a TurbiScan MA 2000 instrument. The rate was highly dependent on the fatty acid/resin acid ratio. A narrow two phase region was found where a lamellar liquid crystalline phase formed by neutral solubilize and soaps was in equilibrium with very dilute solutions. This could be utilized to improve separation by means of a controlled addition of the neutral component.

Keywords Kraft cooking, extractives, solubilization, lamellar phase, sodium oleate, resin acid

Resin plays an important role in the pulping and papermaking process, both as an important by-product ("tall oil") used as a raw material for organic chemicals, such as surfactants and adhesives, and as a source of process instabilities and unwanted deposits on process equipment and in products ("pitch problems"). Concomitantly with the increased closure of process water circulation and new processes (such as the displacement cooking process) these problems have recently become accentuated. The separation of the major part of the resin ("crude tall oil," CTO) has been part of the pulping process for a very long time. Tall oil is classified as a renewable bio-oil, and the importance of full recovery will become emphasized as the demand of renewable sources of energy and raw materials for organic chemicals is increased. Thus, recent developments have highlighted the need for a better understanding of the conditions and mechanisms of separation.

Under the strongly alkaline conditions prevailing in the Kraft cooking process, the fatty acid esters are saponified. The resin and fatty acids are fully dissociated and hence highly soluble, forming micelles in the hot solution of lignin and hemicelluloses ("black liquor") ensuing from the cook.1,3

Very early studies of the micellization of such compounds were published by Ekwall and coworkers.1,4,5 On the other hand, there also are very sparsely soluble neutral components