Minimization of Kraft pulp mill air pollution by optimization techniques
by Moun-Shung Mark Chi

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of MASTER 0F SCIENCE in CHEMICAL ENGINEERING
Montana State University

Abstract:
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The mathematical model developed to minimize odorous emission and maximize annual return in a Kraft recovery furnace unit was tested on the tabulated data of G. N. Thoen and his co-workers (1). The results indicated that emission of air pollutant and the annual return were dependent upon operating conditions of the Kraft recovery furnace unit, and the factors such as excess oxygen and secondary air affected both the odorous emission and the annual return from the Kraft recovery furnace unit.

The mathematical model was also used to calculate the heat used to produce steam, losses of material, chemicals recovered, and annual return.

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TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

LIST OF TABLES AND FIGURES

LIST OF TABLES AND FIGURES (continued)

ABSTRACT

An attempt was made to minimize the air pollution and maximize the return of a Kraft recovery furnace unit under various operating conditions. A mathematical model was set up by employing stoichiometry and thermodynamics to determine the chemical and thermal performance as well as the annual profit return from the Kraft recovery furnace unit. A computer program was written to calculate the factors of interest.

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INTRODUCTION

Over sixty percent of the United States' supply of wood pulp is produced by the Kraft pulping process. But the process, especially the Kraft recovery furnace unit, creates an air pollution problem by discharging hydrogen sulfide, methyl mercaptan, sulfur dioxide, and other sulfur-containing gases into the atmosphere. In addition to the air pollution problem, it results in a chemical and heat loss. Since the Kraft recovery furnace unit releases a large volume of odorous gases and fumes, scrubbing and furnace operations are very difficult.

The recovery cycle of the Kraft pulping process makes the process profitable and also creates an air pollution problem. The recovery cycle is shown in Figure 1. In the Kraft pulping process, wood chips are cooked with a solution of caustic soda and sodium sulfide to remove the lignin from the cellulose fibers. The pulp is then separated from the cooking solution or black liquor. The cooking chemicals in the black liquor are recovered to make the process economical and to solve the disposal problem.

During the recovery operation, weak black liquor is concentrated from approximately 17% solids to about 50% solids in multiple effect evaporators. Further concentrating from 50% solids to 70% solids is carried out in direct contact evaporators using the hot flue gases of the recovery furnace. In this operation, sodium sulfate is added to the strong black liquor making up for chemicals lost in the process. The concentrated black liquor is then burned in the recovery furnace to

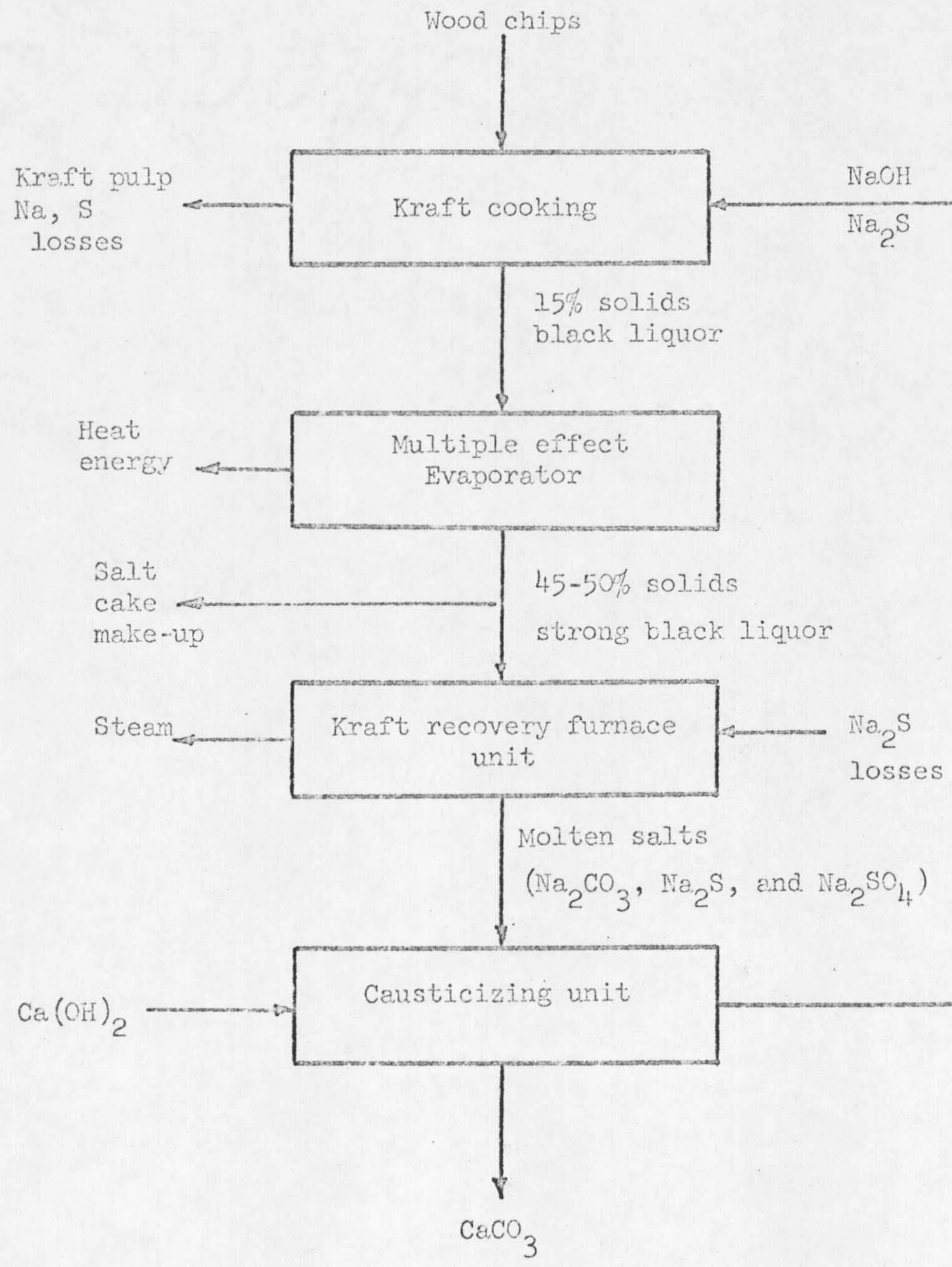

Figure 1. Kraft Recovery Cycle.

recover a portion of the heat by oxidation of the organic material and to recover chemicals in the form of molten salt. The molten salt consists of sodium carbonate and sodium sulfide and a minor amount of sodium sulfate. The recovered chemicals are then reused in the process.

In order to solve this complex air pollution problem, a literature survey was first made to obtain all of the operating conditions that affect the release of odorous compounds.

Irwin B. Douglass made studies in the area of the emission sources (2). He discussed the chemistry involved in odor formation and in the destruction of malodorous compounds by burning, chlorination and treatment with ozone. He suggested that continuous monitoring of the stack gases for hydrogen sulfide would give the greatest promise for minimizing the emission of malodors.

Murray and Rayner (3) concluded that the direct contact evaporator was a source of hydrogen sulfide atmospheric contamination. They found that emission of hydrogen sulfide in the stack gases of the Kraft recovery furnace unit was favored by high concentration of sulfide ion and low pH level in the liquor, and by low concentration of hydrogen sulfide in the flue gases entering the direct contact evaporator.

Hendrickson and Harding (4) pointed out that black liquor oxidation reduced malodorous gas emission of the Kraft recovery furnace. According to Landry and Logwell (5), the oxidation of black liquor prior to burning in the recovery furnace led to large reduction in sulfur-containing gases discharged to the atmosphere and therefore improved the chemical recovery.

Thomas and his co-workers (6) made an investigation into the understanding of the furnace operation from both a chemical and an engineering point of view. They were able to explain the pyrolysis and the combustion of black liquor. Although the explanation was made on an experiment conducted in a laboratory instead of in a Kraft recovery furnace itself, they suggested that the same mechanism actually occurred in the furnace. They proposed that the combustion of black liquor in the recovery furnace consisted of the following steps:

1. The concentrated black liquor was sprayed into the recovery furnace. Water in the black liquor was evaporated.

2. Then the high temperature in the recovery furnace caused the black liquor solids to pyrolyze. The products of pyrolysis of black liquor are low molecular weight hydrocarbons, sulfur-containing compounds, and sodium-containing compounds.

3. Finally, the combustion of pyrolysis gases destroyed most of the low molecular weight hydrocarbons and sulfur-containing compounds. Incomplete combustion of pyrolysis gases caused a serious air pollution problem.

Thoen and his co-authors (1) investigated odorous emission in the Kraft recovery furnace stack gases under various combustion conditions. They indicated that the operating conditions affecting the air pollutant emission were excess oxygen, turbulence, percent of secondary air, and fineness of the black liquor spray. They also found that when the SO_2-H_2O concentration was minimized, indicating sufficient oxygen and good turbulence, the steam production was maximized for a given rate of feed.

In this work, a mathematical model based on engineering principles was developed to solve the air pollution problem economically. The mathematical model was used to find the best operating conditions for maximizing recovery of chemicals and heat, and minimizing the cost for air pollution control.

RESEARCH OBJECTIVES

The main objective of this research project was to develop a technique in the form of a mathematical model to find the optimum operating conditions for air pollution control on Kraft recovery furnace stack gases. Optimum operating conditions are those which give the minimum air pollution and the maximum chemical and heat recovery from the Kraft recovery furnace unit.

The most important consideration of this research project is to solve the complex problems of heat and mass balance, and predict the annual return from the Kraft recovery furnace unit for given operating conditions and, as a result, find the optimum operating conditions by utilizing available data.

THEORY AND ASSUMPTION

The mathematical model developed to optimize the Kraft recovery furnace unit operation relating to air pollution is based upon engineering principles, thermodynamics, and reasonable assumptions. The mathematical model serves as a tool to find the best operating conditions for the Kraft recovery unit in that it gives maximum annual return and minimum air pollution. The model also enables us to analyze the performance of the Kraft recovery furnace unit.

Kraft Recovery Furnace Unit

The Kraft recovery furnace unit is shown schematically in Figure 2. The heat generated in the Kraft recovery furnace is used for the chemical reactions taking place in the furnace and for steam production. The chemicals recovered are reused in the Kraft pulping process. Therefore, the function of Kraft recovery furnace units is to recover chemicals and produce steam from black liquor.

During combustion of black liquor in the furnace, the water in the black liquor is evaporated and the carbonaceous matter formed in the process of cooking wood chips in the digester is burned. The inorganic chemicals in the black liquor are fused and the sodium sulfate in the presence of carbon and a reducing atmosphere is reduced to sodium sulfide. The recovered chemicals in the form of molten salt are sodium carbonate, sodium sulfide, and a small amount of sodium sulfate. The recovered chemicals are further processed in the caustizing process to produce white liquor (NaOH and Na_2S).