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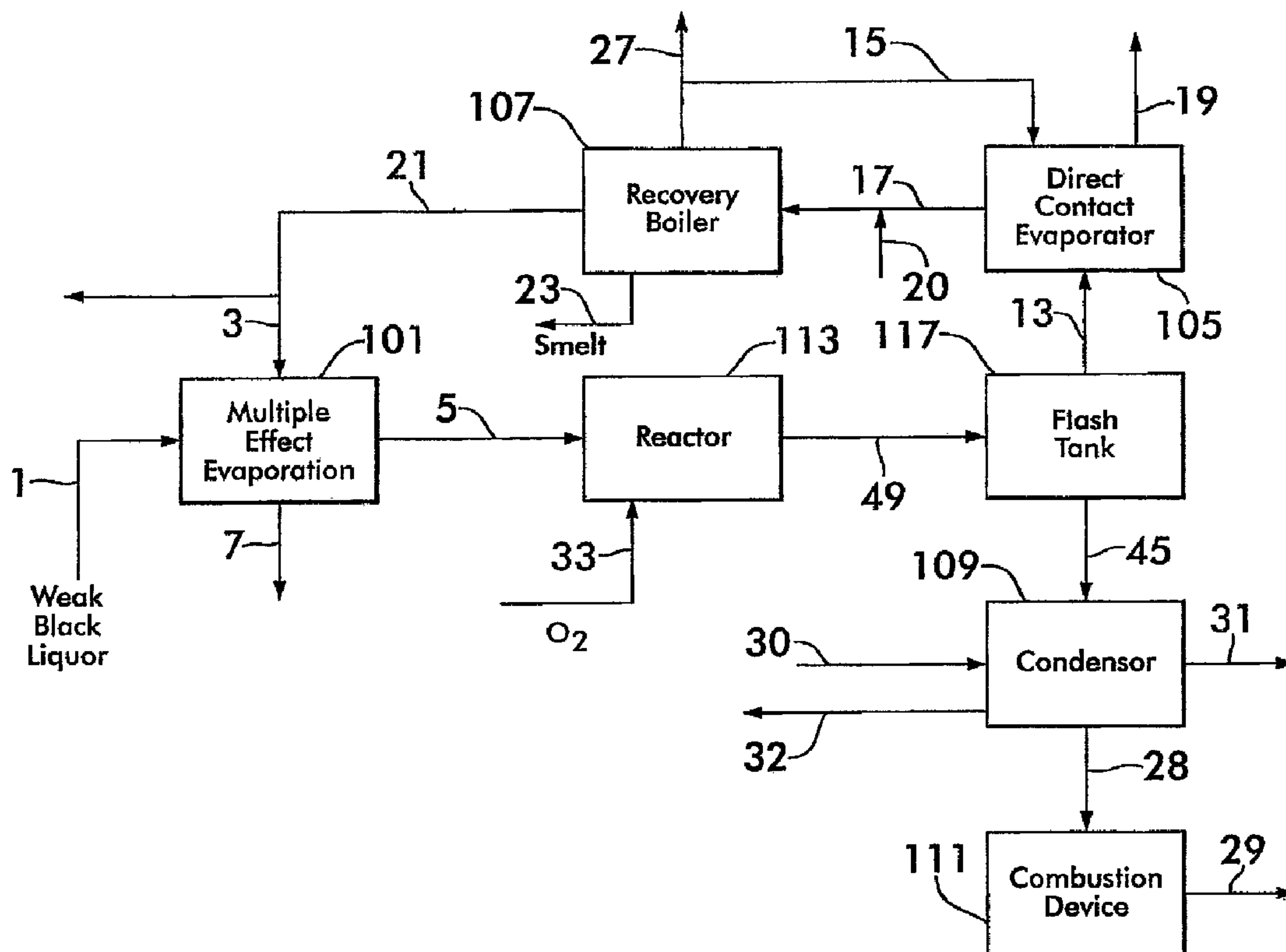
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(54) Titre : METHODE DE REDUCTION DES EMISSIONS POLLUANTES DANGEREUSES D'UN PROCEDE DE RECUPERATION DE PAPIER KRAFT

(54) Title: METHOD TO LOWER THE RELEASE OF HAZARDOUS AIR POLLUTANTS FROM KRAFT RECOVERY PROCESS



(57) Abrégé/Abstract:

A method for removal of pollutants from a pulping process byproduct liquor, the method comprising injecting an oxygen-containing gas into said liquor and condensing the water vapor from the stripping gas so as to produce a condensate comprising pollutants.



(57) **Abrégé(suite)/Abstract(continued):**

Also a method of controlling the flow rate and/or temperature of a pulping process byproduct liquor, the process comprising injecting an oxygen-containing gas into the liquor in a reactor, processing the liquor in a flash tank so as to create a cooled liquor and combining at a least a portion of the cooled liquor with new liquor as the new liquor enters, or while the new liquor is in, the reactor.

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ABSTRACT

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A method for removal of pollutants from a pulping process byproduct liquor, the method comprising injecting an oxygen-containing gas into said liquor and condensing the water vapor from the stripping gas so as to produce a condensate comprising pollutants. Also a method of controlling the flow rate and/or temperature of a pulping process byproduct liquor, the process comprising injecting an oxygen-containing gas into the liquor in a reactor, processing the liquor in a flash tank so as to create a cooled liquor and combining at a least a portion of the cooled liquor with new liquor as the new liquor enters, or while the new liquor is in, the reactor.

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TITLE OF THE INVENTION:

METHOD TO LOWER THE RELEASE OF HAZARDOUS AIR POLLUTANTS FROM
KRAFT RECOVERY PROCESS

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BACKGROUND OF THE INVENTION

The present invention is directed toward the reduction of hazardous air pollutants and reduced sulphur compounds from a byproduct stream produced in a pulping process which contains water where a portion of the water is removed in a multiple effect evaporation system and a further portion of the water is removed in a direct contact evaporator (DCE).

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The Kraft pulping process produces cellulose fibers and black liquor. Black liquor is a water based mixture of organic wood derivatives and alkaline pulping chemicals, chiefly containing degraded lignin, organic acid salts, resin, sodium hydroxide, and sodium salts including carbonate, sulfide, sulfate, sulfite, and thiosulfate. Trace compounds in the black liquor include, methanol, benzene, methyl mercaptan and dimethyl disulfide. Weak black liquor contains 15 wt% dissolved and suspended solids of which about 80% are organic and the remainder are inorganic compounds.

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Weak black liquor is concentrated to about 45-50 wt% solids by multiple effect evaporation and further evaporated to about 65 wt% solids in a Direct Contact Evaporator (DCE), where the liquor is contacted with the flue gases from the recovery boiler. The concentrated liquor is combusted in a recovery boiler to raise steam and to recover sulfur and sodium for reuse in the pulping step. Oxidation of the sodium hydrosulfide in the black liquor is necessary prior to its introduction into the direct contact evaporator to minimize the emissions of hydrogen sulfide in the flue gas from the recovery boiler. Newer mills have replaced direct contact evaporators with indirectly-heated concentrators, which substantially reduces the total reduced sulfur emissions in the flue gas of the recovery boiler.

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Most oxidation processes use air as the oxidant. In these processes the liquor from the

multiple effect evaporators is conveyed to an atmospheric reaction vessel where air is sparged through the liquor and a portion of the oxygen in the air reacts with the sulfide in the liquor to produce sodium thiosulphate. Unreacted oxygen, nitrogen, water vapor and volatile compounds, which have been transfer from the black liquor to the gas phase, are typically vented to the atmosphere. The volatile compounds include methanol and benzene, which are considered hazardous air pollutants (HAP), and methyl mercaptans and dimethyl disulfide, which are considered total reduced sulfur (TRS) pollutants. The total amount of HAP and TRS emissions in the vent of the air oxidizer is a function of their concentration in the black liquor entering the oxidation system, the amount of air used in the process and the amount of oxygen that reacts with the black liquor.

After the oxidation step, the liquor is conveyed to the direct contact evaporator where the liquor contacts the hot flue gases from the recovery boiler. This process humidifies the flue gas and concentrates the black liquor. A portion of the remaining volatile compounds in the black liquor are transferred to the gas phase and discharged to the atmosphere in the flue gas from the DCE. Hydrogen sulphide can also be produced and transported to the gas phase via the reaction $\text{NaSH} + \text{H}_2\text{O} \Rightarrow \text{H}_2\text{S}_{(g)} + \text{NaOH}$. The amount of $\text{H}_2\text{S}_{(g)}$ produced is a function of the concentration of NaSH in the black liquor. The total amount of HAP and TRS emissions in the flue gas is primarily a function of the concentration of these compounds in the liquor entering the DCE. The total amount of HAP and TRS emissions from the combination of air oxidizer and DCE are primarily a function of their concentration in the black liquor from the multiple effect evaporators.

An alternative to the air oxidation process is described in U.S. patent 4,239,589, and 4,313,788, which discloses the oxidation of black liquor in which high recovery of the heat of reaction is accomplished by integration with multiple effect evaporator stages. The process uses a gas with a high concentration of oxygen, typically greater than 99%. The oxidized liquor from the evaporators is typically sent to storage and then passed to the DCE. The higher

5 concentration of HAP and TRS in the black liquor entering the DCE as compared to black liquor from an air oxidation system results in a proportionate increase in the transfer of these compounds to the flue gas from the DCE. Therefore it is generally believed that the total emissions of HAP and TRS from the DCE will be approximately equal to the amount emitted from the combination of an air oxidation system and a DCE.

10 It is a generally desirable to minimize the emission of HAP and TRS compounds into the atmosphere. As a result, Kraft pulp mills consider methods of reducing these emissions. Two identified methods to lower these emissions are the collection and incineration of the vent gas from the air oxidation system or conversion of the DCE recovery boiler to a low odor configuration. Unfortunately both options are expensive.

15 Improved methods of reducing the total HAP and TRS emissions from the recovery area of a pulp mill are needed. The present disclosure and the claims, which follow, describe such an improved method.

As much as the background of the invention described above and the details of the invention described below relate the Kraft pulping process, it is to be understood that there are
20 other pulping processes, such as soda pulping that do not use sulfur in the process and therefore do not require the oxidation of a byproduct stream for odour control. However, these processes typically produce a byproduct stream which is subject to concentration in a multiple effect evaporator system and a direct contact evaporation system and in which there are HAP. In this regard, the present invention can be employed to decrease the HAP in the byproduct
25 stream fed to the DCE thereby reducing the HAP emissions from the DCE.

BRIEF SUMMARY OF THE INVENTION

In one general aspect, the invention is an improvement in a pulping process that employs a multiple effect evaporator such that said evaporator produces a byproduct liquid, the improvement comprising: a) injecting an amount of oxygen-containing gas into a reactor containing the byproduct liquor, the gas comprising oxygen, the oxygen at a concentration of at least 22% (v/v), such that the injecting results in greater than 40% of the oxygen reacting with the components of the liquor and such that the reacting results in an increased temperature of the liquor; b) immediately following step (a), flashing the liquor to generate both a further concentrated liquor and a stripping gas comprising both water vapor and methanol that was in the liquor prior to step (a), wherein the amount of methanol in the stripping gas is controlled by controlling the amount of the oxygen-containing gas injected into the reactor; c) separating the stripping gas from the further concentrated liquor; d) condensing the water vapor from the stripping gas so as to produce a condensate comprising the methanol; and e) treating the further concentrated liquor in a direct contact evaporator.

The invention is expressed in terms of methanol. However, the concentration of many other pollutants in the liquor will be decreased as that of methanol is decreased.

The measurement of the percentage of oxygen that reacts can be calculated based on knowledge of the amount of oxygen that is inputted in step (a) and the amount of unreacted oxygen that is expelled as vent gas from the condensor that condenses the flash tank vapor. Oxygen content of a vent gas can be achieved by well known techniques. (For example, a Servomex oxygen analyzer which employs

the paramagnetic property of oxygen.)

In particular embodiments increasing concentrations of oxygen and/or the percentage of oxygen reacting with the liquor and/or the total amount of oxygen
5 reacting with the liquor may be appropriate. As elaborated upon elsewhere herein, it can be commercially advantageous, to react as much of the oxygen-containing gas with the liquor as possible so as to minimize the amount of unreacted gas that has to be expelled from the system as vent gas – while preferably still effectively removing methanol from, or decreasing its concentration in, the liquor.

10 Particular embodiments of the invention can be summarized as situations where the oxygen-containing gas comprises at least 70% (v/v) oxygen (at least a high percentage), where the oxygen-containing gas comprises at least 95% (v/v) oxygen (a very high percentage), where the percentage of oxygen reacting is at least 70%, where the percentage of oxygen reacting is at least 95%, and
15 combinations thereof.

In some embodiments, the oxygen-containing gas comprises an inert gas at a concentration of 1% to 40% v/v.

In many preferred embodiments, the liquor contains about 40%-55% solids (w/w).

20 In one preferred embodiment, step (a) is done at a temperature less than 175°C.

In many preferred embodiments, subsequent to step (a) the liquor is processed in a flash tank so as to produce a further concentrated liquor and both

water vapor and methanol and wherein said water vapor is condensed to produce a condensate comprising said methanol, and wherein said condensate is separated from said further concentrated liquor.

In one preferred embodiment, the oxygen-containing gas in step (a) is the oxygen-rich gas, and at a time prior to step (a), there is a step comprising injecting an oxygen-containing gas into said concentrated liquor, said gas being the oxygen-poorer gas by virtue of the fact that it contains a lower percentage of oxygen than the oxygen-rich gas does. The oxygen-poorer gas can be air.

In another preferred embodiment, the method further comprises combining, with new byproduct liquor that has not yet been processed through steps (a) and (b), at least a portion of the further concentrated liquor so as to create a mixture of said new byproduct liquor and said portion of further concentrated liquor and, subsequent to said combining, processing at least a portion of said mixture through the steps (a), (b) and (c) described for a byproduct liquor.

In another preferred embodiment, the majority of inert gases and unreacted oxygen in the oxygen-containing gas are separated from the by-product liquor at a point subsequent to reaction of the oxygen at a pressure of greater than 2 bar(g).

There is also disclosed an improvement in a pulping process that employs a multiple effect evaporator such that said evaporator produces a byproduct liquor, the improvement comprising controlling the flow rate and/or temperature of the byproduct liquor, said improvement comprising: a) injecting an oxygen-containing gas into said liquor, said liquor being in a reactor designed for said purpose; b) subsequent to step (a), processing the liquor in a flash tank so as to create a cooled liquor; and c) combining at least a portion of said cooled liquor with new liquor either

previous to said new liquor entering, as said new liquor enters, or while said new liquor is in, said reactor; wherein step (a) is done at temperatures less than 175°C.

In preferred embodiments, step (a) is done at a temperature less than 175°C most preferably at a temperature in the range 120 to 135°C.

5 In preferred embodiments, the pulping process is one in which the oxidation of the liquor takes place in a pressurized reactor operating at greater than 2.0 bar (g).

In other particular embodiments, the oxygen-containing gas comprises at least 70% (v/v) oxygen, more preferably, at least 95% (v/v) oxygen. Similarly, additional particular embodiments are where the liquor contains about 30%-55%
10 solids (w/w).

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Brief Description of the Drawings

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FIG. 1 is a schematic flow diagram of a prior art method of black liquor oxidation, concentration and combustion, which utilizes direct contact evaporation prior to the recovery boiler, wherein the oxidation process uses air and the vent gases from the oxidation process are collected, cooled and incinerated.

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FIG. 2 is a schematic flow diagram of a prior art method of black liquor oxidation, concentration and combustion, which utilizes direct contact evaporation prior to the recovery boiler, wherein the oxidation process uses oxygen and the oxidation process is performed within the multiple effect evaporator system.

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FIG. 3 is a schematic flow diagram of the present invention, which is an improvement to the prior art method of reducing HAP and TRS emissions.

FIG 4 shows a relationship between MeOH and vent flow based on an EPA-Model BLO unit and conditions specified elsewhere herein.

FIG 5 shows a relationship between energy recovery and vent temperature based on an EPA-Model BLO unit and conditions specified elsewhere herein.

FIG 6 shows a relationship between MeOH and vent flow under conditions according to the present invention as specified elsewhere herein.

FIG 7 is a schematic flow diagram of the present invention regarding a method of controlling the flow rate and/or temperature of the black liquor.

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FIG 8 is a schematic diagram of an aspect of the present invention combining the advantages of Figures 3 and 7.

FIG 9 is a schematic diagram of a variation of the invention illustrated in Figure 3.

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DETAILED DESCRIPTION OF THE INVENTION

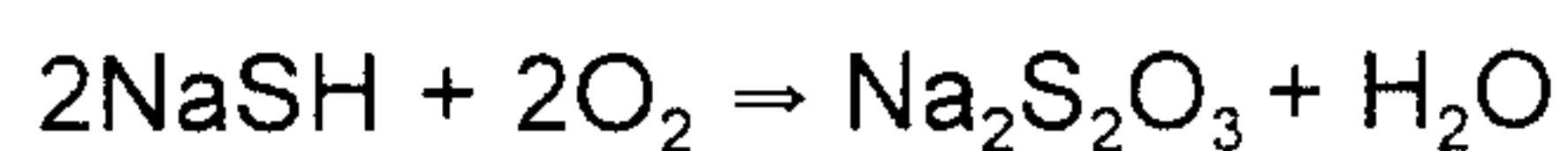
The invention is an improved method of reducing the emissions of HAP and TRS from the recovery area of a pulp mill. The improvement comprises contacting the black liquor, which has been processed through the multiple effect evaporators, with an oxygen-
10 containing gas wherein the oxygen concentration of the gas is at least 22%. At least 40% of the oxygen is made to react with compounds in the black liquor and the heat of reaction is used to produce a stripping gas of sufficient temperature and volume to transfer a substantial portion of the HAP and TRS compounds from the black liquor to the gas phase. Optionally, a flash tank can be used in the process at a point subsequent to the reactor so
15 as to produce the majority of the stripping gas. The amount of stripping gas and hence the amount of HAP and TRS transferred to the gas phase is controlled by varying the amount of oxygen fed to the system and/or the amount of oxygen reacted and/or the concentration of oxygen in the gas. The gas phase, which is primarily water vapour, is cooled whereupon the majority of the water vapor is condensed. A large portion of the HAP, primarily
20 methanol, and a portion of the TRS compounds are transferred to the condensed water vapor (i.e., condensate). The remaining low volume gas stream is discharged to the atmosphere or conveyed to a combustion source for incineration. The volume of gas in the cooled vent stream is controlled by choosing an appropriate oxygen concentration in the oxygen-containing gas and designing the reactor to react with a specific percentage of the
25 injected oxygen. The volume of gas in the vent stream can be controlled to ensure that the concentration of combustible gases is below the lower flammability limit thereby allowing for their discharge into a High Volume, Low Concentration, Non-Condensable (HVLC- NCG) gas system or can be controlled such that the concentration of oxygen in the vent stream is below the minimum oxygen concentration to support combustion, whereupon the vent can

5 be discharged into a Low Volume, High Concentration, Non-Condensable (LVHC-NCG) gas system.

The present invention allows for the controlled removal of HAP and TRS compounds from the black liquor while producing a specific volume of cooled vent gas. The process depends particularly on the knowledge that the concentration of HAP, primarily methanol, in
10 a stripping gas is sensitive to the temperature of that gas.

The improvement of the present invention over the prior art of air oxidation can be understood by an initial review of FIG. 1 Referring to FIG. 1, weak black liquor **1** from the wood pulping and washing steps is fed to multiple effect evaporation system **101**. Weak black liquor contains water, dissolved lignin and other wood constituents, sodium salts (particularly sodium
15 sulfide and other unoxidized sulfur compounds), and sodium hydroxide. Trace compounds in the black liquor include HAP such as, methanol, and benzene, and TRS such as methyl mercaptan and dimethyl disulfide. The liquor is typically at 90°C and 1.5 bar(g), and typically contains 15 wt% solids. The liquor is concentrated in multiple effect evaporator system **101** heated by steam **3** as is known in the art to yield partially concentrated black liquor **5** and
20 residual steam/condensate **7**. A portion of the HAP and TRS compounds in the weak black liquor are transferred to the steam/condensate **7** and a portion remain in the partially concentrated black liquor **5**.

The partially concentrated black liquor **5**, typically at 90°C and 1.0 bar(g) containing typically 48 wt % solids flows to air black liquor oxidation system **103** in which air **9** oxidizes the sodium
25 hydrosulfide to sodium thiosulphate via the reaction:



and a portion of the organic material in the black liquor.

The amount of air sparged into the liquor is controlled so as to convert at least 95% of the sodium hydrosulfide to sodium thiosulphate. The percent of oxygen in the air **9** that specifically
30 reacts with black liquor is typically no greater than 40%. To achieve a NaSH concentration of less

5 than 2g/l in the black liquor a significant excess of air **9** is required and the percent of oxygen in the air that reacts with the black liquor is generally no greater than 30%.

Unreacted oxygen, the nitrogen in the air, water vapour, and HAP and TRS compounds are vented **11** from the reactor to a heat transfer device **109**, herein called a condensor, where the gas **11** is cooled and a portion of the water vapor and HAP and TRS are condensed and
10 discharged from the condensor in stream **32**. The cooled vent gas **28** flows to a combustion device **111** where the HAP and TRS compounds are incinerated and the products of combustion **29** are discharged to the atmosphere. The concentration of volatile compounds, including methanol, benzene, acetaldehyde, acetone, methyl mercaptans, and dimethyl disulfide, in the vent gas **11** is a function of thermodynamic equilibrium. The total amount of
15 these compounds in the vent gas **11** is dependent upon their concentration in the feed black liquor **5**, the amount of air fed **9** to the oxidizer system, the temperature of the feed black liquors and the amount of oxygen reacted.

Oxidized black liquor **13**, now containing typically less than 2g/l of sodium sulfide, and a lower concentration of HAP and TRS compounds, passes to the direct contact evaporation
20 system **105** in which the black liquor is further concentrated by direct contact with hot flue gas **15** from recovery boiler **107**. Fully concentrated black liquor **17** and final flue gas **19** flow from the evaporator system **105**. Flue gas **19** contains, water vapor, combustion products, hydrogen sulfide and HAP and TRS compounds. The concentration of HAP and TRS compounds in the flue gas **19** is a function of thermodynamic equilibrium. The total amount of these compounds
25 in the flue gas **19** is dependent primarily upon their concentration in the feed black liquor **13**.

The black liquor at this point typically contains 65 wt% solids at 115°C. Fully concentrated black liquor **17** is combined with sodium sulfate (salt cake) makeup **20** and passes into recovery boiler **107** in which the organic materials are combusted with air to generate heat withdrawn as steam **21** for use elsewhere in the mill. The inorganic sulfur, largely sodium thiosulfate is
30 reduced to sodium sulfide in the boiler and smelt **23**, containing molten sodium sulfide and

sodium carbonate, is withdrawn for preparing green liquor. Flue gas streams **27** and **19** pass to a cleanup system for particulate removal typically an electrostatic precipitator. The oxidation of sodium sulfide in black liquor oxidation system **103** is required in order to reduce the amount of hydrogen sulfide formed in direct contact evaporator **105** and carried therefrom to the atmosphere in final flue gas **19**.

Data on the concentration and the total emissions of HAP and TRS from an air oxidizer **103** and a DCE **105** have been collected. In the EPA document entitled 'Chemical Recovery Combustion Sources at Kraft and Soda Mills' data is presented on the emissions of Hazardous Air Pollutants from air oxidation systems and direct contact recovery boilers. Emissions from Air-sparging BLO systems were 2.03×10^{-4} kilograms per kilogram of black liquor solids (Kg/Kg) of which, 1.73×10^{-4} Kg/Kg was methanol (i.e., 85%). HAP emissions in the flue gas from direct contact recovery boilers were 4.32×10^{-4} Kg/Kg of which, 1.70×10^{-4} Kg/Kg was methanol (i.e., 39%). TRS emissions from Air-sparging BLOX systems are estimated to be 2.93×10^{-5} Kg/Kg, based on data in the document. TRS emissions, of which the majority is $\text{H}_2\text{S}_{(g)}$, from the DCE boiler are estimated to be 1.21×10^{-4} Kg/Kg.

Further data was compiled by the National Council of the Paper Industry for Air and Stream Improvements Inc. in Technical Bulletin No. 680 entitled: 'Volatile Organic Emissions from Pulp and Paper Mill Sources, Part VI- Kraft recovery furnaces and black liquor oxidation systems'. In this document, the emissions from 2 air oxidation systems and 2 direct contact evaporator recovery boilers were presented.

The HAP emissions from the air oxidation system at a mill designated Mill D were 1.85×10^{-4} Kg/Kg of which, 1.65×10^{-4} Kg/Kg was methanol (i.e., 89%). The HAP emissions from the recovery boiler of Mill D were 1.00×10^{-4} Kg/Kg of which 0.65×10^{-4} Kg/Kg was methanol (i.e., 65%).

The HAP emissions from the air oxidation system at a mill designated Mill H were 1.40×10^{-4} Kg/Kg of which, 1.05×10^{-4} Kg/Kg was methanol (i.e., 75%). The HAP emissions from the

5 recovery boiler of Mill H were 1.40×10^{-4} Kg/Kg of which 1.0×10^{-4} Kg/Kg was methanol (i.e., 71%).

The above data is summarized in Table I.

Table I. Values are in Kg/Kg black liquor solids (BLS)

	EPA	Mill D	Mill H
Air Oxidizer Vent			
HAP	2.03×10^{-4}	1.85×10^{-4}	1.40×10^{-4}
MEOH	1.73×10^{-4}	1.65×10^{-4}	1.05×10^{-4}
TRS	2.93×10^{-5}		
DCE Flue Gas			
HAP	4.32×10^{-4}	1.00×10^{-4}	1.40×10^{-4}
MEOH	1.703×10^{-4}	0.65×10^{-4}	1.00×10^{-4}
TRS	1.21×10^{-4}		

Data on vent gas volumes are presented in the NCASI report. Models of air sparged black liquor oxidation systems are presented in the EPA report that specifies the flow of black liquor solids, the vent gas flow rate, the moisture content of the vent gas and the methanol emissions in kg/day.

The data is summarized in Table II.

Table II

	Black Liquor Firing Rate Kg/day	Vent gas Flow Dry Standard m3/sec	Moisture Content %	Methanol Emissions Kg/d
EPA	1.2	7.3	35	212
Mill D	0.76	4.19	54	124
Mill H	1.175	2.84	44.6	101.6

A thermodynamic analysis based on the operating conditions as specified in the EPA model was conducted to estimate the concentration of methanol in the feed black liquor 5 to the air oxidizer and the amount of oxygen in the air 9 that reacts with the black liquor. The estimated

5 MeOH concentration in the black liquor was 150mg/l and approximately 19.2% of the total oxygen in the air (i.e., 1186kg/hr) was estimated to react with compounds in the black liquor.

A thermodynamic analysis was conducted to estimate the total amount of methanol that would be transferred to the flue gas of the DCE if the air oxidation system was eliminated. It was found that the total emissions increased by an amount which was almost equal to the
10 amount of methanol in the vent of the air oxidizer.

Maximizing the amount of HAP and TRS in the vent gas from an air oxidizer, which is subsequently collected and incinerated, would be advantageous, as it would lower the HAP and TRS emissions from the DCE. One potential means of increasing the total amount of HAP and TRS in the vent is through an increasing in the amount of air 9 fed to the air oxidation system.

15 However, there are distinct limits to this approach. It is known that the amount of oxygen reacting with the black liquor 5 fed to an air oxidation system is primarily dependent upon the size of the atmospheric reaction vessel and the amount of material in the black liquor that can be oxidized at the operating temperature of the air oxidizer. Therefore, an increase in airflow to the oxidizer will not cause an proportionate increase in the amount of oxygen reacted. As
20 a result, the temperature of the vent gas and the liquor will decrease due to the cooling effects of humidification. Equilibrium calculations show that the concentration of HAP in the vent gas, primarily methanol, declines with a decrease in vent temperature. This is illustrated in FIG. 4 where data from the EPA model was used wherein the black liquor solids in the feed liquor 5
25 was 50mt/hr, the concentration of black liquor solids in the feed black liquor 5 was 48 wt%, the moisture content of the vent gas 11 was 35 wt% and the vent gas volume 11 at 54°C was 12.7m³/sec. Based upon this data the estimated concentration of MeOH in the feed

liquor 5 was 150mg/l, and the air flow 9 was 8.16m³/sec. The air flow 9 was varied and the new equilibrium methanol concentration and flow rate of the vent gas 11 were calculated. The total amount of oxygen in the air 9 reacting with the black liquor was constant at 1186kg/hr. The
30 x-axis in Fig. 4 represents the ratio of vent gas flow to black liquor solids flow. The y-axis

5 represents both the equilibrium methanol concentration in ppm, (dashed line), and the total
emission of methanol in kg/hr, (solid line), in the vent gas **11**. It can be seen that the
concentration of methanol declines as the vent gas flow is increased. This decline diminishes
the positive impact of a higher vent gas volume on the transfer of HAP and TRS to the gas
phase. Under these particular conditions, an increase in vent flow from 0.75 m³/kg BLS to
10 1.4m³/kg BLS, an 87% increase, causes an increase in total methanol in the vent stream from
8.65 kg/hr to 9.07kg/hr, a 4.9% increase. Typically, the potential reduction in HAP and TRS
emissions from the DCE resulting from an increase in the air oxidizer vent gas flow does not
justify the cost to collect, cool and incinerate the additional vent gas.

An additional drawback of the prior art is poor energy recovery. The amount of energy
15 recovered from the vent gas **11** is dependent upon the temperature of the gas **28** exiting the
condensor. This is illustrated in FIG. 5 which is based on the EPA model. The x-axis is the
temperature of the gas exiting the condensor. The y-axis represents the amount of energy
transferred from the feed vent gas **11** to the cooling medium **30**, which is normally water. At
most Pulp mills there is an excess amount of warm water **31** and in many cases, water at a
20 temperature of less than 60°C has no value.

Therefore, generally there is limited value in the energy recovered from an air oxidizer
vent gas.

An additional drawback of this prior art is the large volume of cooled vent gas **28** and
the high HAP and TRS concentration in the cooled vent gas **28**. Equilibrium calculations were
25 conducted based on the EPA model with the assumption that the cooled vent gas **28** is cooled
to 54°C. At these conditions, the cooled vent gas **28** flow rate was 12.7m³/sec and
approximately 82% of the methanol entering the condensor in stream **11**, remained in the
cooled vent gas stream. Vent gas stream **28** is then passed directly to combustion device
111 or discharged into the High Volume Low Concentration, Non-condensable gas system
30 (HVLC-NCG). The combustion device is typically an existing unit at the mill such as a power

& steam boiler, the recovery boiler, or an independent incinerator. The high volume of the cooled vent gas stream **28** requires large diameter ducting to transfer the gas to the combustion device, and the high moisture content and low oxygen content of the stream can cause operational problem in the combustion device or in the case where the combustion
5 device is a dedicated incinerator, there is a substantial capital investment requirement.

EXAMPLE 1

The present invention comprises improvements to the prior art methods of Fig. 1 and Fig. 2. One embodiment of the invention is illustrated in Fig. 3. Partially concentrated black liquor **5**, which has been processed through the multiple effect evaporators **101**, is passed to
10 a reactor **113** where the liquor is pressurized and an oxygen containing gas **33** having a concentration of 95% is injected into the stream. 99% of the oxygen is made to react with the sulfide and organic material in the black liquor causing an increase in the sensible heat of the black liquor. The oxidized liquor **49** is then depressurized in flashtank **117** where the sensible heat is converted to latent heat in the form of water vapor. A portion of the HAP
15 and TRS compounds in the liquor are transferred to the gas phase due to thermodynamic equilibrium. The vent gas **45** is conveyed to a condensor **109** where the gas is cooled and the majority of the water vapour is condensed and removed in condensate stream **32**.
Additionally, the majority of the methanol and some of the HAP and TRS are condensed and discharged in the condensate stream **32**. The vent gas exiting the condensor **28** is
20 discharged to atmosphere or conveyed to an incineration device **111** or discharged into either the HVLC-NCG system or the low volume, high concentration non-condensable gas system (LVHC-NCG). The desired total amount of HAP and TRS transferred to the vent gas is controlled through the reaction of a sufficient amount of oxygen **33** with the black liquor **5**.

5 Oxidized black liquor **13**, now containing typically less than 2g/l of sodium sulfide, and
a controlled concentration of HAP and TRS compounds, passes to the direct contact
evaporation system **105** in which the black liquor is further concentrated by direct contact with
hot flue gas **15** from recovery boiler **107**. Fully concentrated black liquor **17** and final flue gas
19 flow from the evaporator system **105**. Flue gas **19** contains, water vapor, combustion
10 products, hydrogen sulfide and HAP and TRS compounds. The concentration of HAP and TRS
compounds in the flue gas **19** is a function of thermodynamic equilibrium. The total amount of
these compounds in the flue gas **19** is dependent primarily upon their concentration in the feed
black liquor **13**, which concentration is controlled through the adding of a specific amount of
oxygen **33**.

15 The fully concentrated black liquor **17** proceeds in the same manner as described in the
prior art.

An improvement of the present invention over the prior art of air oxidation comprises the
ability to control the transfer of HAP and TRS into the vent gas **45** by controlling the amount
of oxygen **33** reacting with the black liquor **5**. This is illustrated in FIG. 6 where data from the
20 EPA model was used. In this graph, the x-axis represent the ratio of vent gas flow **45** of the
invention and vent gas flow **11** of the prior art to black liquor solids flow. The y-axis represents
the total transfer of methanol in kg/hr from the black liquor to the air oxidation system vent
stream **11** and the present invention vent stream **45**. In the present invention, 9kg/hr of
methanol can be transferred to the vent gas **45** at a total vent gas ratio of 0.4m³/kg BLS. In
25 contrast, the vent flow **11** from the air oxidation system must be 1.2m³/kg BLS to transfer the
same 9Kg/hr. Also, in the present invention, the reaction of a sufficient amount of oxygen **33**
to produce a vent stream volume of 0.6 m³/kg BLS will cause a transfer of 10kg/hr of methanol
to the vent stream **45** whereas it is clear from the data that an air oxidation system cannot
achieve this amount of transfer.

An additional improvement to the prior art of air oxidation is a significantly lower cooled vent gas flow **28** as compared to the vent flow **28** FIG. 1 from an air oxidation system. Equilibrium calculations were conducted based on the EPA model parameters with the assumption that the cooled vent gas **28** is cooled to 54°C. At these conditions, the present invention cooled vent gas **28** flow rate was less than 0.035 m³/sec and approximately 1% of the methanol entering the condensor in stream **45**, remained in the cooled vent gas stream **28** whereas the cooled vent gas **28** flow rate from the air oxidation system was 12.7 m³/sec and approximately 82% of the methanol entering the condensor in stream **45**, remained in the cooled vent gas stream **28**. This very low flow gas stream from the present invention, which has been depleted in oxygen can be discharged safely into the existing low volume, high concentration, non-condensable gas system LVHC. The gases of the LVHC system are typically combusted in the lime kiln at a Kraft mill. Therefore no additional incineration device is required.

An additional improvement of the present invention is the recovery of the energy in the vent gas **45** at a temperature that is sufficiently high to be of value to the mill. In the presented embodiment, the flashtank **117** is operated at 1.0 bar(g). At this pressure approximately 98% of the energy in the vent gas is recovered at a temperature of approximately 90°C, thereby providing energy at a temperature that is of value to the mill. Alternatively, should a mill desire to recover the energy at a higher temperature, the flashtank can be made to operate at a higher pressure. This option is unavailable in an air oxidation system as the cost to operate the system at pressure would be prohibitively high.

The improvement of the present invention over the prior art as described in US patents 4,239,589 and 4,313,788 can be understood by an initial review of FIG. 2. Referring to FIG. 2, weak black liquor **1** from the wood pulping and washing steps is fed to multiple effect evaporation system **101**. Weak black liquor contains water, dissolved lignin and other wood constituents, sodium salts (particularly sodium sulfide and other unoxidized sulfur

5 compounds), sodium hydroxide. Trace compounds in the black liquor include HAP such as, methanol, and benzene, and TRS such as methyl mercaptan and dimethyl disulfide. The liquor is typically at 90°C and 1.0 bar(g), and typically contains 15 wt% solids. The liquor is concentrated in multiple effect evaporator system 101 heated by steam 3 as is known in the art to yield partially concentrated black liquor 13 and residual steam/condensate 7. In the
 10 prior art, a liquor stream 47 is withdrawn from an intermediate location in the multiple effect evaporators 101. The withdrawn liquor 47, typically at 110°C and 2.0 bar(g) containing 35 wt % solids flows to a reactor 113 where a gas stream 51 containing typically 99% oxygen, oxidizes the sodium hydrosulfide to sodium thiosulphate via the reaction:



15 and a portion of the organic material in the black liquor.

The prior art specifically directs that the amount of oxygen made to react with the black liquor should be sufficient to convert a desired amount of NaSH to Na₂S₂O₃. The oxidized liquor 49, which is now at an elevated temperature, is returned to the multiple effect evaporators 101 where the sensible heat in the liquor is converted to latent heat in the effect
 20 receiving the heated black liquor. The liquor proceeds through the remaining effects of the multiple effect evaporators 101 and is discharged as partially concentrated and oxidized black liquor 13, typically at 100°C and 1.0 bar(g) containing 48 wt % solids.

A portion of the HAP and TRS compounds in the weak black liquor 1 are transferred to the steam/condensate 7 and a portion remain in the partially concentrated black liquor.

25 Oxidized black liquor 13, now containing typically less than 2g/l of sodium sulfide, passes to the direct contact evaporation system 105 in which the black liquor is further concentrated by direct contact with hot flue gas 15 from recovery boiler 107. Fully concentrated black liquor 17 and final flue gas 19 flows from the evaporator system 105. Flue gas 19 contains, water vapor, combustion products, hydrogen sulfide and HAP and
 30 TRS compounds. The concentration of HAP and TRS compounds in the flue gas 19 is a

5 function of thermodynamic equilibrium. The total amount of these compounds in the flue gas 19 is dependent primarily upon their concentration in the feed black liquor 13 which concentration is dependent upon the operating conditions of the multiple effect evaporators.

The fully concentrated black liquor 17 proceeds in the same manner as described in FIG. 1.

10 In the practice of this prior art, the concentration of HAP and TRS compounds in the liquor entering the direct contact evaporator system 105 is equal to the concentration in the liquor exiting the multiple effect evaporation system 101. As a result, the amount of HAP and TRS emissions from the DCE 105 is greater than the prior art of air oxidation or the present invention.

15 The improvement of the present invention over this prior art comprises the ability to substantially lower the HAP and TRS emissions from the DCE 105 by conducting the oxidation after the multiple effect evaporation system and by controlling the amount of oxygen reacting with the black liquor so as to control the transfer of HAP and TRS into vent gas 45, FIG.3.

20 EXAMPLE 2

This example shows how a combination of oxygen based and air based black liquor oxidation can be used to maximize the stripping of HAP's and TRS from the black liquor.

25 The removal of methanol from the liquor is a function of the temperature of the vent gas. To achieve a low Na₂S concentration a mill normally has 2 oxidizers, a primary and a secondary. The primary oxidizer converts about 90% of the Na₂S and the percent of oxygen fed to the system, which reacts with the liquor, is high (i.e., 35%). This means the energy release per volume of vent gas is high (again on a relative basis). Therefore the temperature of the primary oxidizer vent will be reasonably high and thus the methanol

30

5 stripped from the liquor (as Kg MeOH/Kg vent flow) will be high. In contrast, the amount of
feed oxygen reacting with the liquor in the 'secondary' oxidizer is quite low. This means that
the temperature of the vent stream is generally lower than the feed temperature of the black
liquor (i.e., the energy needed to humidify the vent is greater than the energy released in the
oxidation reaction). Therefore, the amount of methanol (HAP's) stripped from the liquor into
10 the vent of the secondary oxidizer is low (relatively).

This issue is further addressed in this Example and is illustrated in Fig. 9. One uses a
certain amount of air (as the primary oxidant) in a primary air oxidizer 127, and then
replaces the second oxidizer with an oxygen-based reactor 113, which is connected to the
air oxidizer by line 50. In this way, the total amount of vent gas 45 for an equal transfer of
15 HAP's from the liquor would be less than an oxidation system employing secondary oxidizer
However, the cost is a factor. The primary reason to go to the oxygen process is to minimize
the cooled vent stream from the condensor. If one opts for the above, the vent flow will be a
function of the amount of 'air' oxidation employed. Since the cost of collection and
incineration is high, due consideration must be made to the capital and operating costs.

20 EXAMPLE 3

The logic is the same as in Example 2. However, one enriches the air stream sent to the
primary air oxidizer. The intent is to maximize the HAP removal while minimizing the vent
25 steam.

EXAMPLE 4

One may not want to use 100% oxygen, but rather prefers to operate at an oxygen
30 concentration such that the nitrogen (argon or other inert gas) that passes through the

5 system and finally into the vent from the condensor in an amount sufficient to ensure that
 the concentration of combustible NCG (primarily methyl mercaptans and dimethyl disulfide)
 is well below the lower flammability limit. One operates at the oxygen concentration that
 dilutes the remaining NCG's to levels below the LFL. If this is not done, one has to add air or
 an inert gas to the condensor to control the concentration of NCG to below the LFL.

10 EXAMPLE 5

The intent of the black liquor oxidation process is to convert NaSH to Na₂S₂O₃. A
 competing reaction is the oxidation of organic material in the black liquor. Both reactions
 15 are exothermic, and cause a rise in liquor temperature. As the temperature increases, the
 amount of oxygen reacting with the organic material increases. Also, the solubility of
 calcium carbonate decreases with temperature. A process has been developed wherein a
 portion of the black liquor is recycled and cooled (by flashing) to controls the temperature of
 the oxidation reaction.

20 When black liquor is oxidized 2 reactions can occur:



Oxygen + Organic $\rightarrow$ acids

It is well known that the amount of oxygen reaction with the organic material in the black
 liquor increases with an increase in reactor temperature. That is to say that the selectivity to
 25 NaSH decreases with increased temperature. Additionally, the solubility of calcium
 carbonate in black liquor decreases with an increase in temperature. Both of these
 temperature effects have caused problems in oxygen based black liquor oxidation systems.

Also, high temperature reduces oxygen solubility and lowers the oxygen partial pressure
 in a closed system, which slows the rate of reaction.

30 The temperature rise in an oxygen based black liquor oxidation system depends

5 upon the amount of oxygen reacted. The amount of oxygen reacted is a function of the NaSH concentration in the liquor. This concentration is dependent upon the amount of water present in the black liquor. From an energy recovery, and environmental perspective, it is best to conduct the oxidation at a solid concentration of between 40 and 60% solids. However, the NaSH concentration at these concentrations is high, at approximately 35g/l. Therefore the temperature rise through the reactor is highest at these solids. The higher temperature lowers the selectivity which in turn increases the amount of oxygen needed for NaSH conversion, which increases the temperature.

To address the foregoing, an oxidation system can be designed which allows for temperature control. The system is illustrated in Fig. 7, for a system using an indirect contact evaporator 106 and in Fig. 8 for a system using a direct contact evaporator 105. A portion of the liquor is recycled using line 123 in Fig. 7 and line 121 in Fig 8, which is otherwise the same as Fig. 3. In Fig. 8, the liquor is cooled by flashing in the flash tank 117 and then reintroduced into the reactor 113.

The advantages of the system include:

- 20 1) Control of the reaction selectivity;
- 2) A means of ensuring that the solubility limit of calcium carbonate in the black liquor is greater than the actual concentration of the calcium carbonate in the black liquor;
- 3) Constant reactor operating conditions; and
- 4) Oxidation of NaSH which is somewhat independent of the flow rate of black liquor to/from the system.

Although illustrated and described herein with reference to certain specific embodiments, the present invention is not intended to be limited to the detailed embodiments shown. One skilled in the art can understand the invention and make various modifications thereto without departing from the basic spirit thereof, and without departing from the scope of the claims which follow.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. In a pulping process that employs a multiple effect evaporator such that said evaporator produces a byproduct liquor, the improvement that comprises:

a) injecting an amount of oxygen-containing gas into a reactor containing said byproduct liquor, said gas comprising oxygen, said oxygen at a concentration at least 22% (v/v), such that said reacting results in an increased temperature of said liquor;

b) flashing said liquor to generate both a further concentrated liquor and a stripping gas comprising both water vapor and methanol that was in the liquor prior to step (a), wherein the amount of methanol in said stripping gas is controlled by controlling the amount of said oxygen-containing gas injected into said reactor;

c) separating said stripping gas from said further concentrated liquor;

d) combining at least a portion of the further concentrated liquor with new byproduct liquor so as to create a mixture of said new byproduct liquor and said portion of further concentrated liquor, and repeating steps (a), (b) and (c) for at least a portion of said mixture.

2. The method of claim 1, wherein said oxygen-containing gas comprises at least 70% (v/v) oxygen.

3. The method of claim 2, wherein said oxygen-containing gas comprises at least 95% (v/v) oxygen.

4. The method of any one of claims 1 to 3, further comprising prior to said injecting step the step of entering the new byproduct liquor into the reactor, and wherein said combining step occurs previous to entering said new byproduct liquor

into the reactor, as said new byproduct liquor enters the reactor or while said new byproduct liquor is in said reactor.

5. The method of any one of claims 1 to 4, wherein after step (c) said method further comprises the steps of:

condensing said water vapor from said stripping gas so as to produce a condensate comprising said methanol; and

treating at least a portion of the further concentrated liquor in a direct contact evaporator.

6. The method of claim 1, wherein said oxygen-containing gas comprises at least 70% (v/v) oxygen and wherein at least 70% of the oxygen in the oxygen-containing gas reacts with the components of the liquor.

7. The method of claim 1, wherein said oxygen-containing gas comprises at least 95% (v/v) oxygen and wherein at least 95% of the oxygen in the oxygen-containing gas reacts with the components of the liquor.

8. The method of any one of claims 1 to 7, wherein the liquor in step (a) contains about 40% -55% solids (w/w).

9. The method of any one of claim 1 to 8, wherein the oxygen-containing gas comprises an inert gas at a concentration of 1% to 40% (v/v).

10. The method of any one of claims 1 to 9, wherein steps (b) and (c) occur in a flash tank.

11. The method of claim 1, wherein the oxygen-containing gas in step (a) is the oxygen-rich gas, and wherein at a time prior to step (a), there is a step comprising injecting an oxygen-containing gas into said byproduct liquor, said gas being the oxygen-poorer gas by virtue of the fact that it contains a lower percentage

of oxygen than the oxygen-rich gas does.

12. The method of claim 11, wherein the oxygen-poorer gas is air.
13. The method of claim 1, wherein the majority of inert gases and unreacted oxygen in the oxygen-containing gas are separated from the byproduct liquor at a point subsequent to reaction of the oxygen at a pressure of greater than 2 bar (g).
14. The method of claim 1, wherein step (a) is done at temperatures less than 175°C.
15. The method of claim 14, wherein step (a) is done at temperatures less than 150°C.
16. The method of claim 14, wherein step (a) is done at temperatures in the range 120 to 135°C.
17. The method of claim 14, wherein the oxidation of the liquor takes place in a pressurized reactor operating at greater than 2.0 bar (g).
18. The method of claim 14, wherein said oxygen-containing gas comprises at least 70% (v/v) oxygen.
19. The method of claim 18, wherein said oxygen-containing gas comprises at least 95% (v/v) oxygen.
20. The method of claim 14, wherein the liquor in step (a) contains about 30%-55% solids (w/w).

FIG. 1
(PRIOR ART)

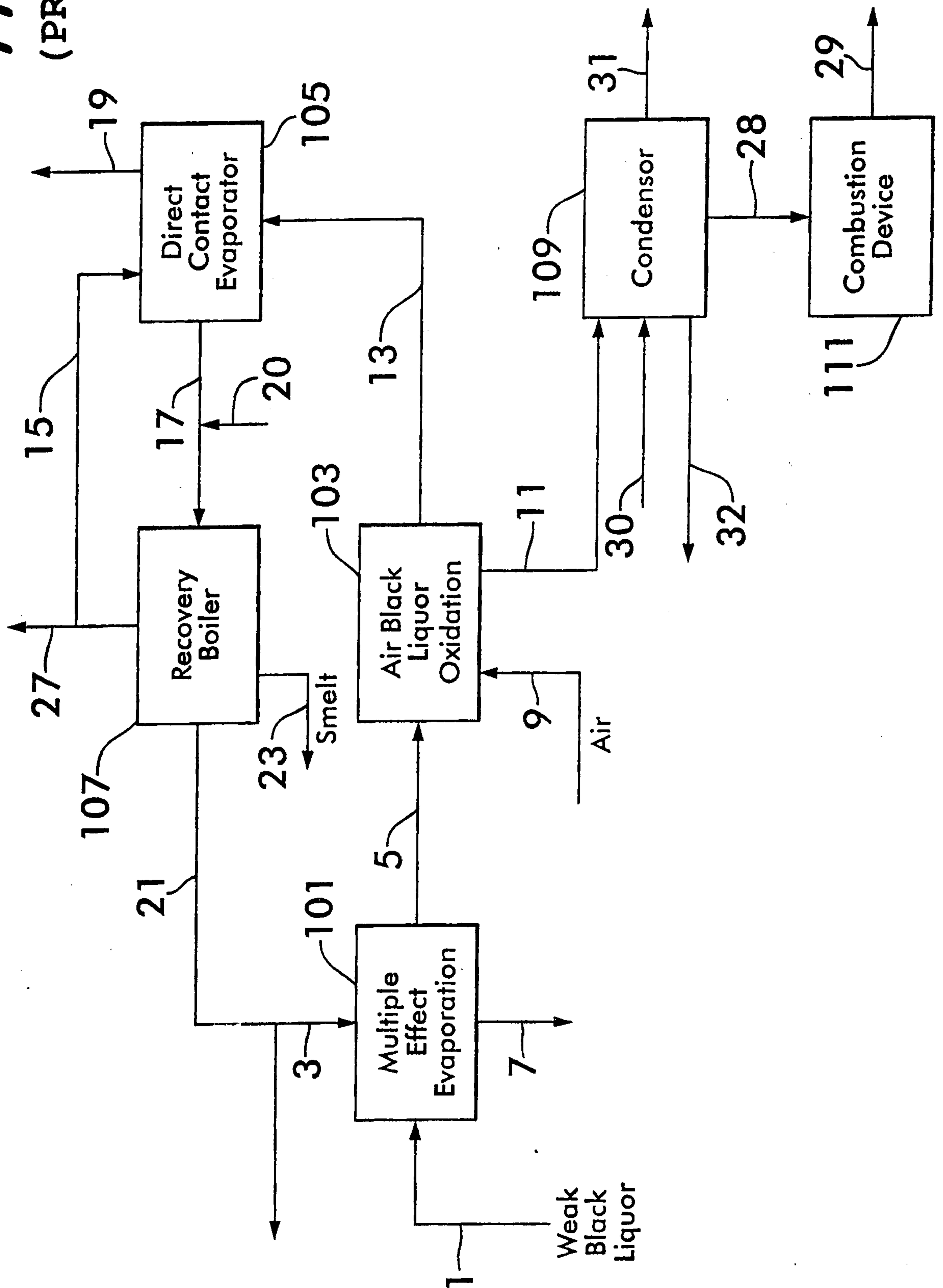
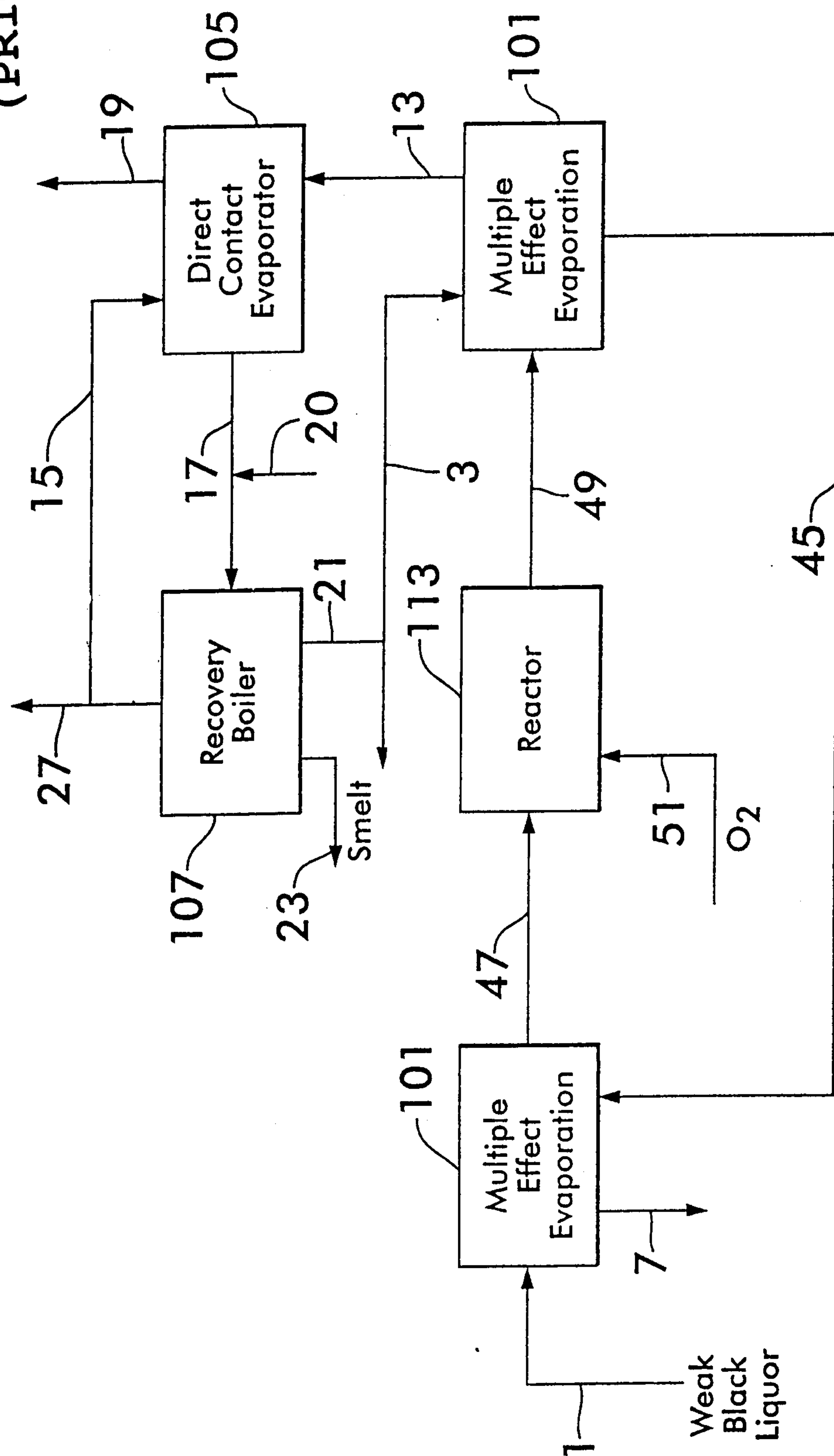


FIG. 2
(PRIOR ART)



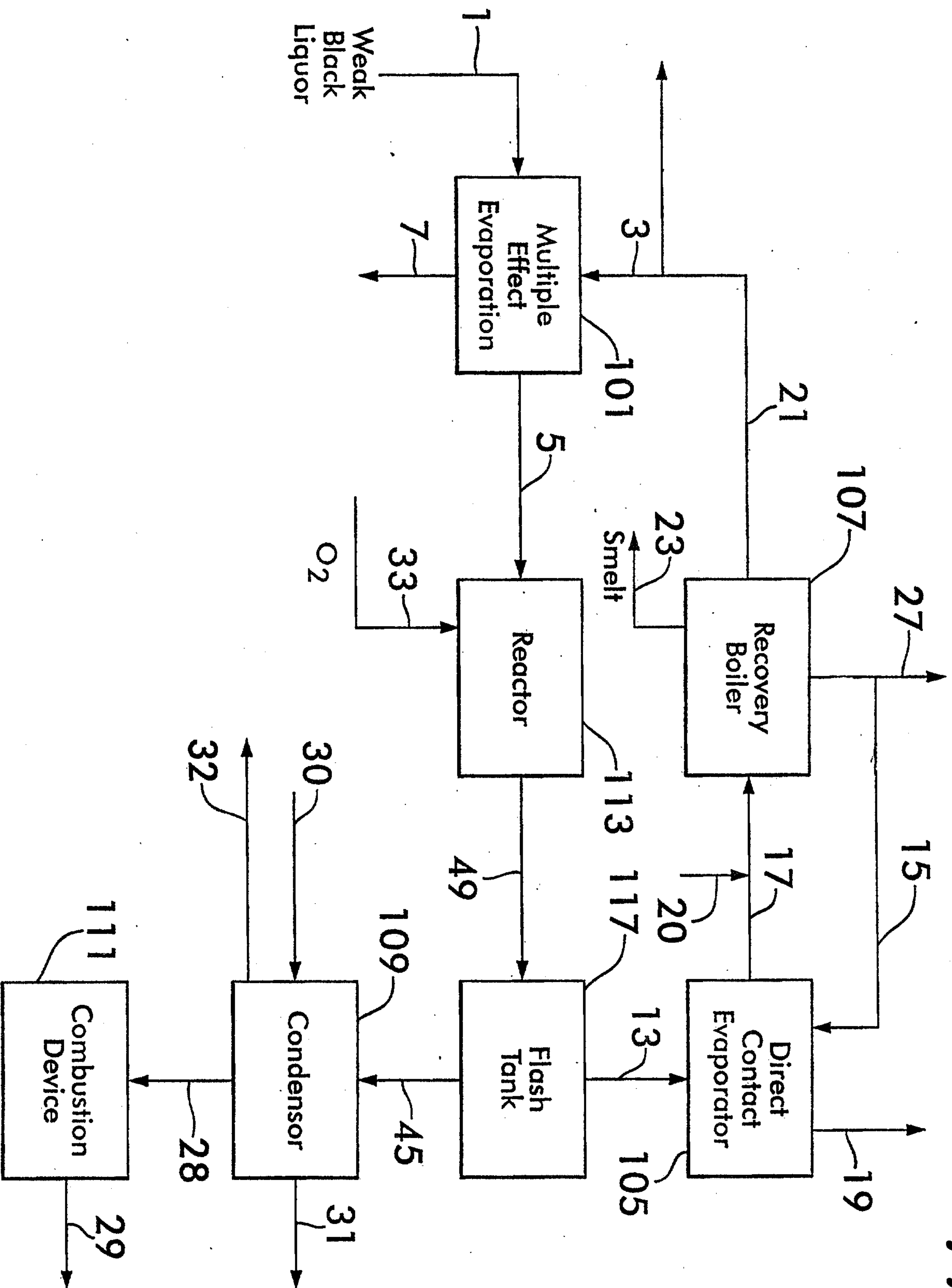


FIG. 3

FIG.4

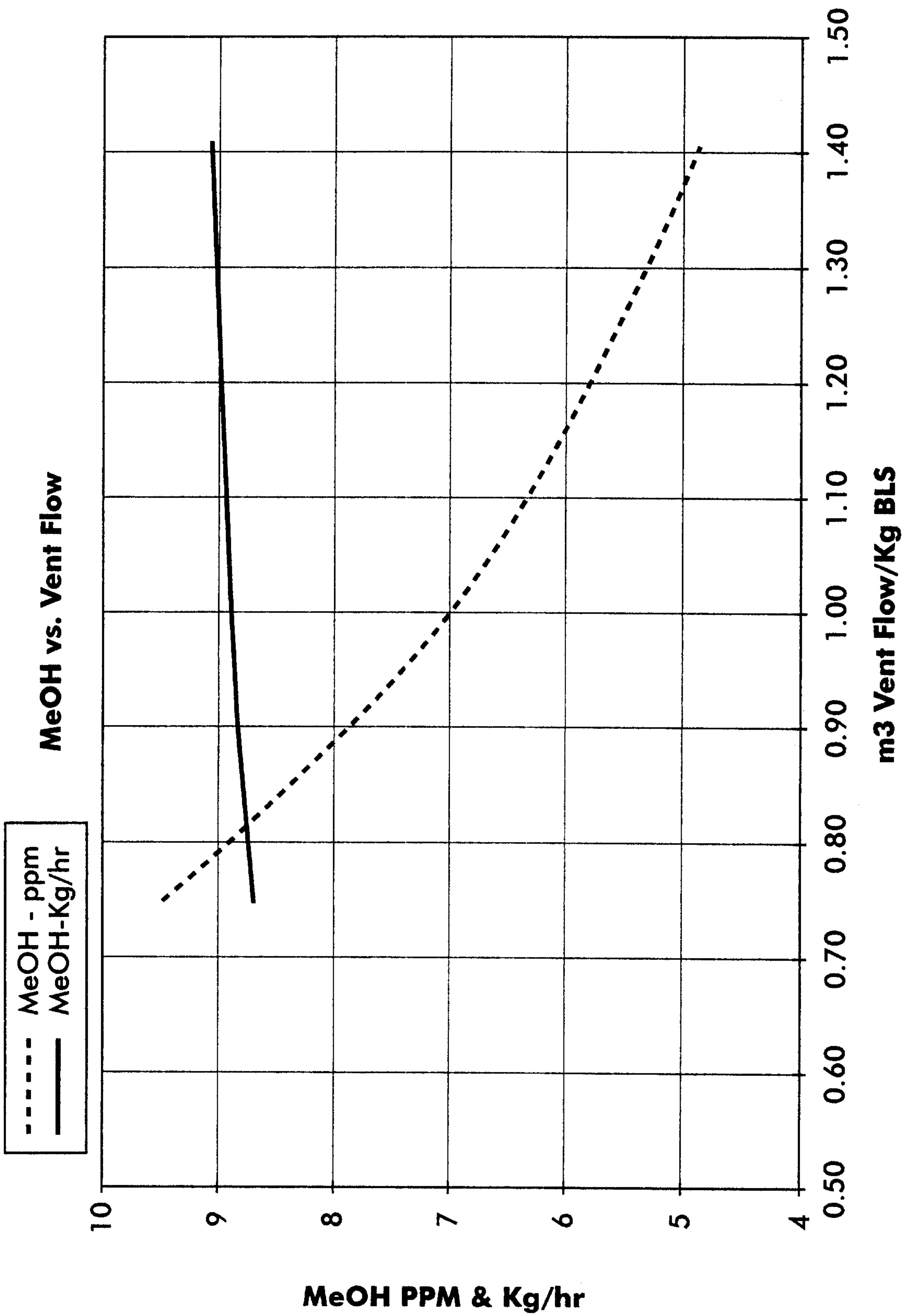


FIG.5

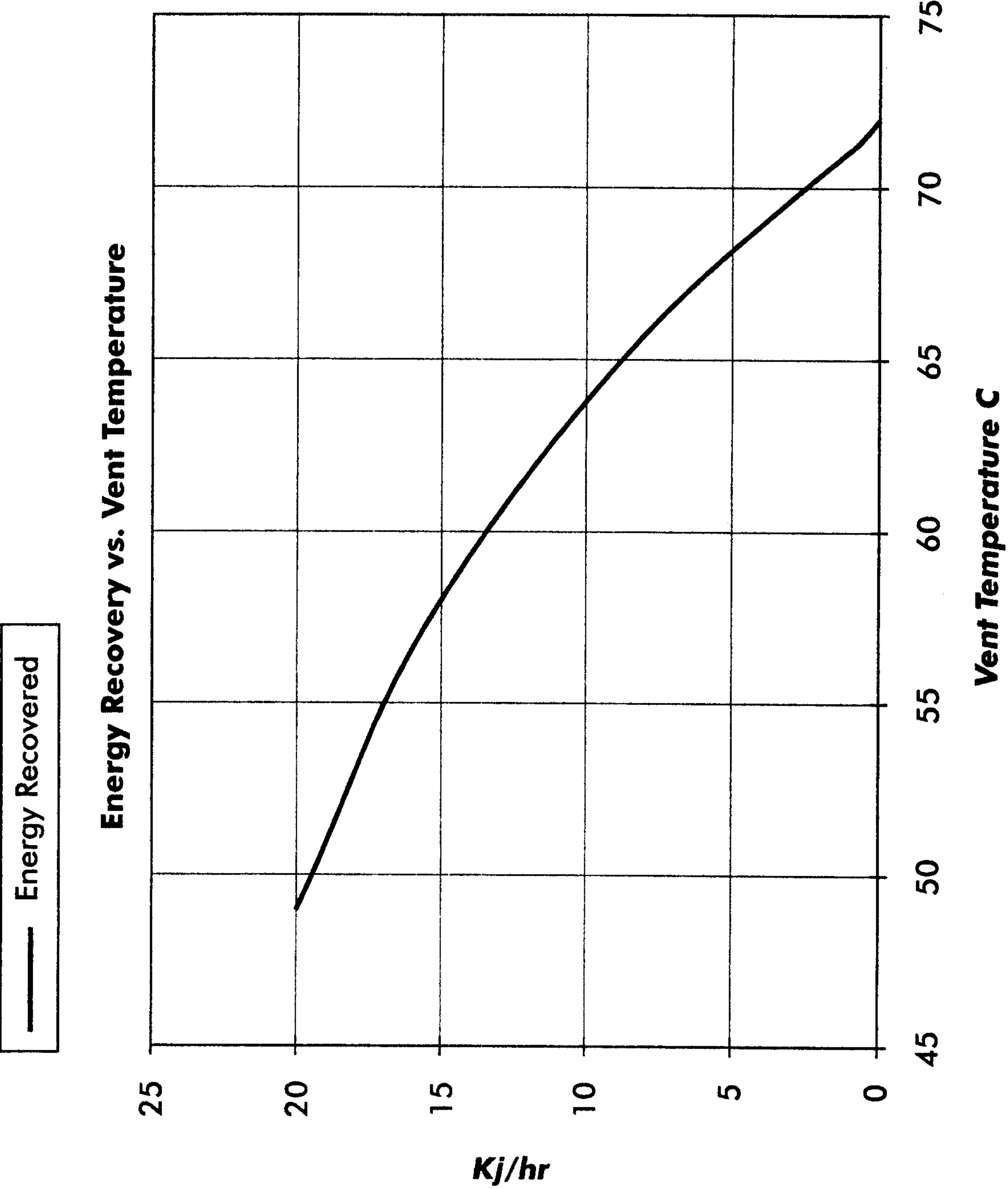
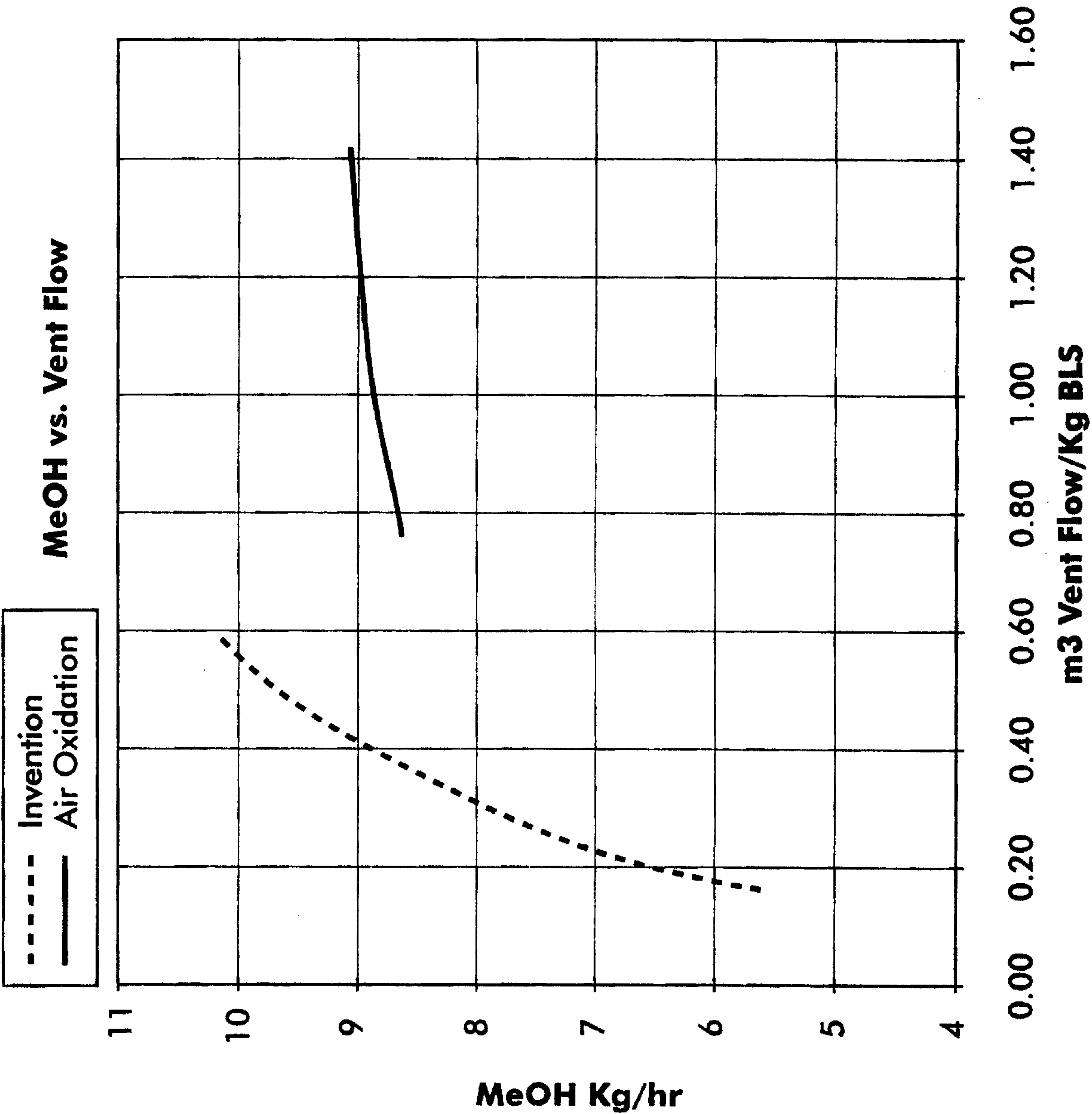


FIG. 6



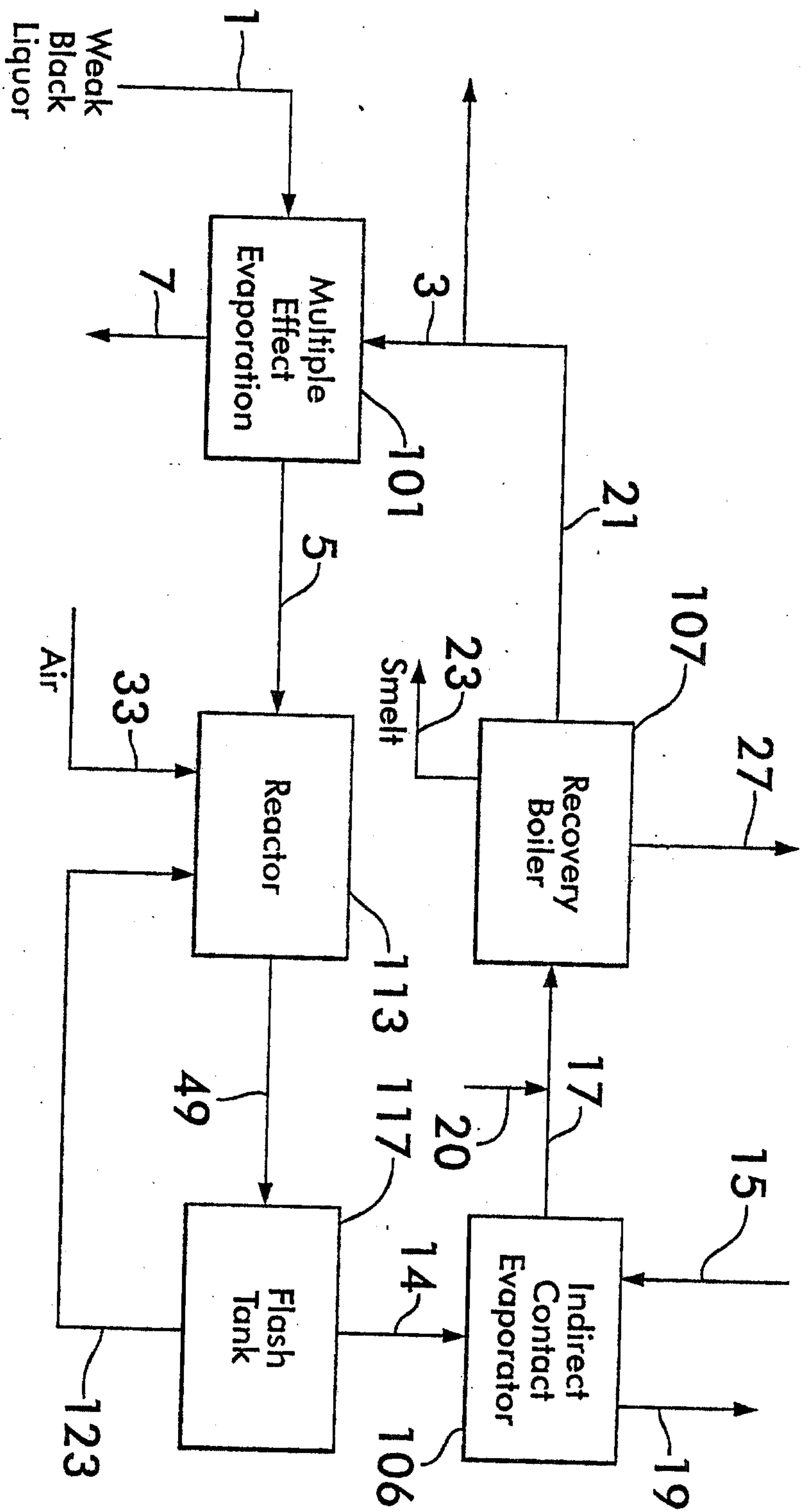
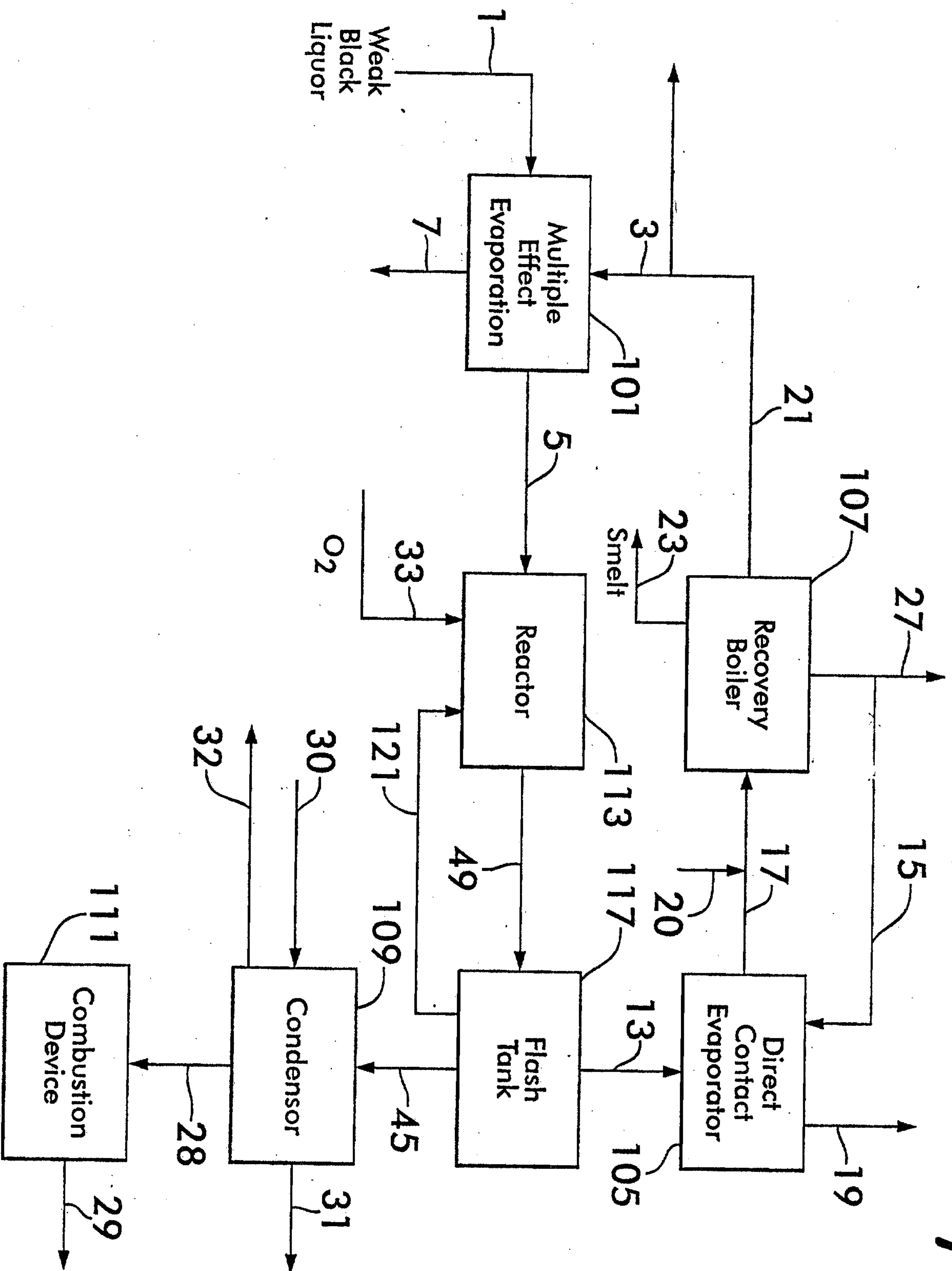


FIG. 7

FIG. 8



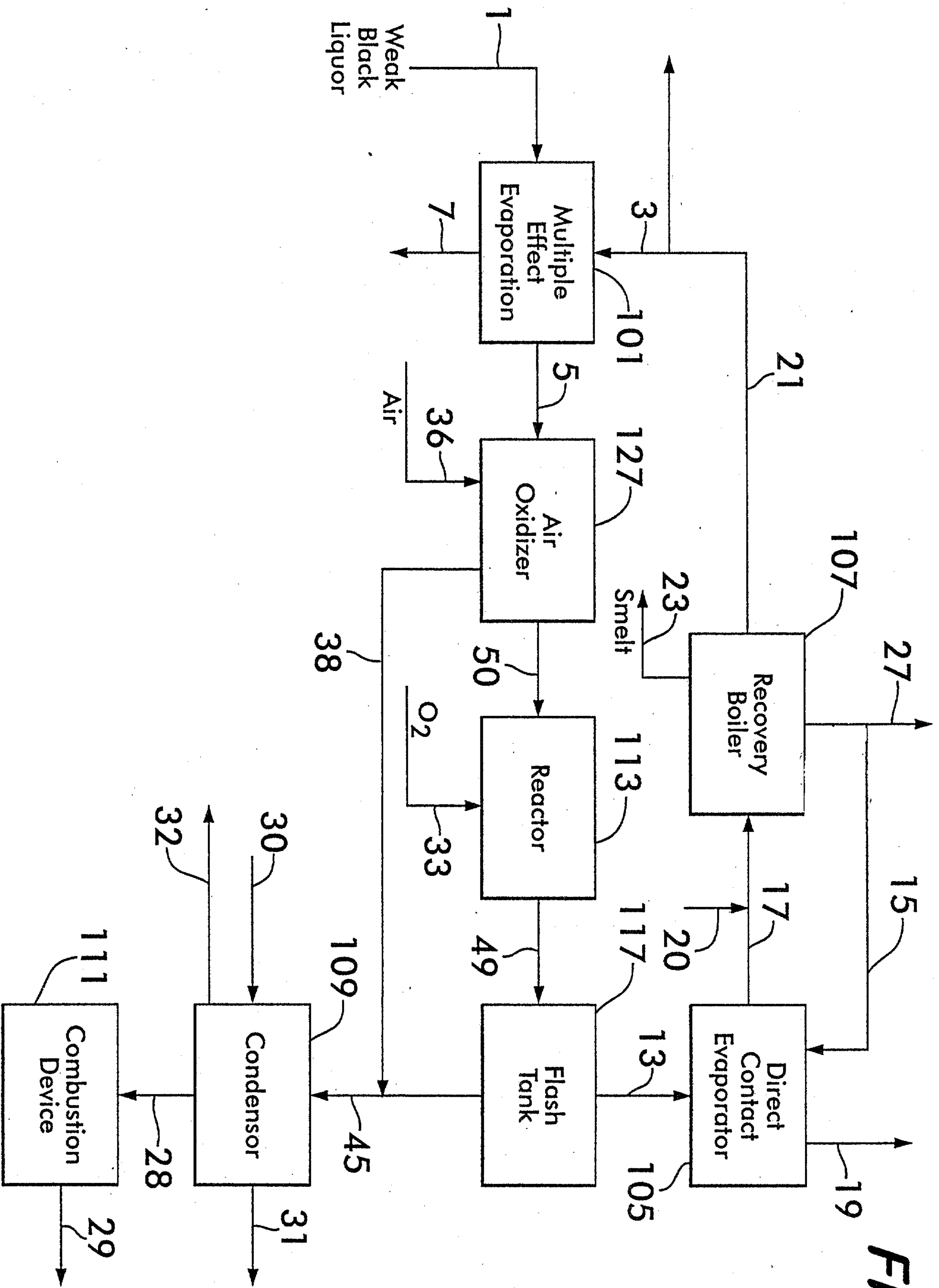


FIG. 9

