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**THE PURIFICATION OF GASEOUS WASTE STREAMS FROM
NITRIC ACID PLANTS WHICH CONTAIN NITROGEN OXIDES ↓**

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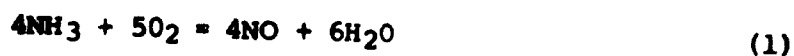
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INTRODUCTION

THE COMMERCIAL MANUFACTURE OF NITRIC ACID IS A THREE STEP PROCESS WHICH IS BASED ON THE FOLLOWING REACTIONS:



THE OXIDATION OF AMMONIA TAKES PLACE OVER A PLATINUM ALLOY CATALYST AND THE REACTION IS VERY RAPID. TYPICAL REACTOR TEMPERATURES ARE 900-930°C. THE EFFLUENT FROM THE REACTOR IS COOLED AND THE NO IS OXIDIZED WITH THE EXCESS OXYGEN IN THE PROCESS STREAM AS THE NO₂ IS FORMED; IT QUICKLY REACHES THE EQUILIBRIUM WITH ITS DIMER, N₂O₄, AND THE STREAM IS FED TO AN ABSORBER. REACTIONS (2), (3) AND (4) CONTINUE THROUGHOUT THE ABSORBER. THE WATER IS INTRODUCED AT THE TOP OF THE ABSORBER AND ADDITIONAL AIR IS ADDED AT THE BOTTOM. REACTION (4) IS PARTIALLY COMPLETED ON EACH ABSORBER TRAY AND THE SPACE BETWEEN THE TRAYS IS USED FOR REACTIONS (2) AND (3). THE GAS LEAVING THE TOP TRAY WHICH IS REFERRED TO AS ABSORBER TAIL GAS CONTAINS APPROXIMATELY 96% NITROGEN, 3% OXYGEN, 0.3% NO_x, AND THE BALANCE IS WATER AND INERTS. NO_x REFERS TO NO, NO₂, N₂O₄, AND SMALL QUANTITIES OF N₂O. THE N₂O IS FORMED AS A BYPRODUCT FROM THE AMMONIA OXIDATION.

THE TAIL GAS HAS A REDDISH-BROWN COLOR AND IS POTENTIALLY TOXIC TO ANIMAL LIFE BECAUSE OF THE NITROGEN OXIDES. TWO OF THESE OXIDES ARE THE MOST DANGEROUS; THESE ARE THE NO AND THE NO₂. THE PURPOSE OF THIS PAPER IS TO DISCUSS A METHOD WHICH WILL REMOVE THESE ENVIRONMENTALLY OBJECTIONABLE MATERIALS FROM THE TAIL GAS. THE METHOD COMBINES A REDUCING FUEL (SUCH AS HYDROGEN OR LIGHT

HYDROCARBONS) AND A PRECIOUS METAL CATALYST TO RESULT IN AN ABATEMENT SYSTEM WHICH NOT ONLY PURIFIES THE TAIL GAS BUT ALSO GENERATES POWER.

THE PAPER IS DIVIDED INTO THREE CHAPTERS AS FOLLOWS: CHEMISTRY AND THERMODYNAMICS, CATALYST AND KINETICS, AND EQUIPMENT DESIGN AND ECONOMICS. IT WILL BE SHOWN THAT THE ABATEMENT SYSTEM CAN BE INSTALLED AT EXISTING PLANTS OR CAN BE INCORPORATED WITH THE DESIGN OF NEW PLANTS. THE SYSTEM NEED NOT BE AN ADD ON COST WITHOUT ANY ECONOMIC BENEFITS. THE ABATEMENT REACTIONS ARE EXOTHERMIC AND EQUIPMENT CAN BE USED TO EXTRACT THE HEAT ENERGY AND CONVERT THE ENERGY TO USEFUL POWER. THE MOST COMMON USE OF THIS POWER IS TO DRIVE AIR COMPRESSORS WHICH SUPPLY THE AIR FOR THE AMMONIA OXIDATION REACTION. AT THIS TIME, CATALYTIC ABATEMENT SYSTEMS ARE BEING CONSTRUCTED IN THE U.S. TO MEET LEGISLATED AIR QUALITY STANDARDS.

I. CHEMISTRY AND THERMODYNAMICS

THERE ARE THREE BASIC REACTIONS WHICH OCCUR IN THE CATALYTIC ABATEMENT REACTOR: THE FIRST TWO REACTIONS ARE RAPID. THE REACTIONS ARE SHOWN WITH CH₄ AS THE FUEL; HOWEVER, HYDROGEN OR OTHER LIGHT HYDROCARBONS MAY BE USED. THE TYPICAL TAIL GAS DISCHARGE FROM A NITRIC ACID PLANT HAS A FAMILIAR REDDISH-BROWN COLOR AND THIS COLOR IS DUE TO THE PRESENCE OF NO₂. ONCE THE NO₂ CONCENTRATION HAS BEEN REDUCED TO APPROXIMATELY 400 PARTS PER MILLION, THEN THE GAS IS NEARLY INVISIBLE.

THE FIRST REACTION,
$$\text{CH}_4 + 4\text{NO}_2 = 4\text{NO} + \text{CO}_2 + 2\text{H}_2\text{O} , \quad (5)$$
 IS CALLED THE DECOLORIZATION REACTION.

THE SECOND REACTION,
$$\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O} , \quad (6)$$
 IS THE COMBUSTION OF OXYGEN. THE REACTION RATE OF THIS REACTION IS PROBABLY THE LARGEST, SINCE THE OXYGEN CONCENTRATION IS AN ORDER OF MAGNITUDE LARGER THAN THAT OF THE NO_x. ON A SPECIFIC RATE BASIS, THE NO₂ AND THE OXYGEN ARE BOTH CONSUMED AT APPROXIMATELY EQUAL RATES. HISTORICALLY, NITRIC ACID PLANTS HAVE INCLUDED CATALYTIC DECOLORIZERS. DECOLORIZERS ARE SIMILAR TO ABATERS WITH THE EXCEPTION THAT THE NO_x CONCENTRATION IN THE TAIL GAS IS NOT LOWERED; THE NO₂ IS REDUCED TO NO AND SOME OF THE OXYGEN IS COMBUSTED. THESE DECOLORIZATION REACTORS OPERATE WITH AN OXIDIZING ATMOSPHERE. IN OTHER WORDS, THERE IS EXCESS OXYGEN PRESENT AT ALL TIMES.

THE THIRD REACTION,
$$\text{CH}_4 + 4\text{NO} = \text{CO}_2 + 2\text{H}_2\text{O} + 2\text{N}_2 , \quad (7)$$
 IS THE ABATEMENT REACTION. THE NO WHICH IS ORIGINALLY PRESENT IN THE TAIL GAS AND THAT WHICH IS PRODUCED BY REACTION (5) IS REDUCED TO ELEMENTAL NITROGEN. THIS REACTION DOES NOT PROCEED AT A SIGNIFICANT RATE UNTIL THE OXYGEN IS COM-

PLETELY REACTED. TO ENSURE THAT THE ABATEMENT REACTION WILL PROCEED, THE REACTORS ARE OPERATED WITH EXCESS FUEL. IF THERE IS SUFFICIENT FUEL AVAILABLE AND IF THE REACTOR IS AT A HIGH TEMPERATURE, ALL OF THE NO CAN BE EXPECTED TO REACT.

THE FUEL USED FOR THE ABATEMENT AND DECOLORIZATION REACTIONS MUST BE A REDUCING AGENT. TYPICALLY, THESE AGENTS ARE HYDROGEN, LIGHT HYDROCARBONS, OR CARBON MONOXIDE, AND PERHAPS THE MOST COMMONLY USED FUEL IS NATURAL GAS. IN MANY CASES, THE NITRIC ACID PLANT IS LOCATED NEAR AN AMMONIA PLANT. THERE ARE TWO FUELS THAT ARE AVAILABLE FROM THE AMMONIA PLANT WHICH MAY BE USED IN THE CATALYTIC ABATER. THESE ARE PURGE GAS FROM THE AMMONIA-SYNTHESIS LOOP OR THE ACTUAL SYNTHESIS GAS. SINCE THE PURGE GAS MUST BE REMOVED FROM THE AMMONIA SYNTHESIS CYCLE, AND GENERALLY THERE IS A SUFFICIENT QUANTITY AVAILABLE, THE PURGE GAS IS FREQUENTLY THE REDUCING FUEL. THE PURGE GAS CONTAINS BOTH HYDROGEN AND METHANE AND THE SYNTHESIS GAS CONTAINS HYDROGEN WITH NO APPRECIABLE QUANTITY OF METHANE PRESENT. IN EUROPE, FREQUENTLY THE MOST PRACTICAL FUEL IS NAPHTHA WHICH IS QUITE SATISFACTORY. THE FUEL CONSUMPTION IS TYPICALLY 10 PERCENT MORE THAN THE STOICHIOMETRIC DEMAND.

THE THREE REACTIONS MENTIONED PREVIOUSLY ARE HIGHLY EXOTHERMIC, AND EACH FUEL HAS A DIFFERENT IGNITION TEMPERATURE IN THE PRESENCE OF THE CATALYST. THE IGNITION TEMPERATURE IS DEPENDENT UPON THE OXYGEN CONCENTRATION IN THE REACTOR FEED STREAM, THE FUEL CONCENTRATION, THE CATALYST METAL, AND THE GAS VELOCITY AND PRESSURE IN THE REACTOR. LABORATORY EXPERIMENTS HAVE BEEN USED TO DETERMINE IGNITION TEMPERATURES FOR THE VARIOUS FUELS. THE INLET GAS TEMPERATURE TO THE REACTOR IS DESIGNED TO BE HIGHER THAN THE IGNITION TEMPERATURE. THIS

"OVERDESIGN" IS TO ENSURE THE CONTINUANCE OF GOOD REACTOR PERFORMANCE AS THE CATALYST AGES, COMMENSURATE WITH WHICH REQUIRED IGNITION TEMPERATURE INCREASES. EACH FUEL HAS A DIFFERENT HEATING VALUE. WHEN CONSIDERING A TAIL GAS OF CONSTANT COMPOSITION, THE TEMPERATURE RISE ACROSS THE CATALYST BED CAN BE READILY CALCULATED FROM THE HEATS OF REACTION AND THE SPECIFIC HEATS OF THE VARIOUS COMPONENTS. TYPICALLY, THE TEMPERATURE RISE WILL BE APPROXIMATELY 400°C. THE IGNITION TEMPERATURE AND TEMPERATURE-RISE ACROSS THE CATALYST BED MUST BE CAREFULLY CONSIDERED IN THE DESIGN OF THE ABATEMENT SYSTEM. THIS DESIGN IS COMPLICATED BY THE VARIATION OF THE TAIL GAS COMPOSITION FROM PLANT TO PLANT. FOR A SPECIFIC PLANT, THE TAIL GAS COMPOSITION CAN VARY FROM SUMMER MONTHS TO WINTER MONTHS. THE AMMONIA OXIDATION CATALYST MUST BE CHANGED FREQUENTLY AND THE ABATER SYSTEM MUST BE DESIGNED FOR CONTINUED OPERATION DURING START-UP AND SHUT-DOWN OF THE PLANT. TABLE I SHOWS VARIOUS FUELS, COMPOSITIONS, IGNITION TEMPERATURES, AND THE ADIABATIC TEMPERATURE RISE PER PERCENT OXYGEN IN THE TAIL GAS.

TABLE I PROPERTIES OF TYPICAL CATALYTIC ABATEMENT FUELS

FUEL NAME	COMPOSITION (1)	IGNITION	TEMPERATURE
	(MOLE %)	TEMPERATURE, °C	RISE (2), °C
NATURAL GAS	99+CH ₄	480-510	128
PURGE GAS	60 H ₂	200	151
	14 CH ₄		
	26 INERTS		
SYNTHESIS GAS	60 H ₂	200	156
	40 INERTS		
NAPHTHA (3)	-	400	-

- NOTES: (1) THE COMPOSITIONS ARE APPROXIMATE
 (2) THIS IS THE ADIABATIC TEMPERATURE RISE PER MOLE % O₂ IN THE TAIL GAS, AND IS BASED ON A TAIL GAS COMPOSITION OF 3% O₂ AND 0.2% NO_x.
 (3) THE COMPOSITION OF NAPHTHA CAN NOT BE CONVENIENTLY EXPRESSED FOR THIS TABLE.

THE MOST CRITICAL TEMPERATURE CONSIDERATION IN THE DESIGN OF THE ABATER IS THE OUTLET TEMPERATURE. THE BULK GAS TEMPERATURE VARIES AS PREDICTED BY HEAT TRANSFER CALCULATIONS. THE REACTOR EFFLUENT TEMPERATURE IS NEARLY THE SAME AS THE TEMPERATURE OF THE CATALYST BED. THIS IS BECAUSE OF THE REACTIONS THAT OCCUR ON THE CATALYST SURFACE SINCE HEAT DISSIPATION AWAY FROM THE CATALYST SURFACE IS MINIMAL, EXPERIMENTS HAVE BEEN CONDUCTED TO DETERMINE THE RELATIONSHIP BETWEEN THE OUTLET TEMPERATURE AND THE EXTENT OF ABATEMENT. (1) THE EXPERIMENTAL RESULTS HAVE BEEN SUMMARIZED AND THEY ARE SHOWN IN FIGURE I.

CATALYTIC ABATERS ARE DESIGNED TO HAVE A MAXIMUM OUTLET TEMPERATURE OF APPROXIMATELY 800°C. THIS IS CLOSE TO THE MAXIMUM ALLOWABLE CONTINUOUS OPERATING TEMPERATURE OF THE CATALYST. GOOD DESIGN DICTATES THAT THE PREHEAT TEMPERATURE BE SUFFICIENTLY HIGH TO ALLOW THE CATALYST TO OPERATE AT A TEMPERATURE OF AROUND 750°C. OPERATION AT THESE HIGH TEMPERATURES ALLOWS GOOD FUEL EFFICIENCY AND ENSURES THAT LOW CONCENTRATIONS OF NITROGEN OXIDES WILL BE EMITTED. THE HIGH TEMPERATURE OPERATION DOES ACCELERATE THE THERMAL DEGRADATION OF THE CATALYST.

II. CATALYST AND KINETICS

THE TAIL GAS ABATEMENT CATALYST IS A METAL FROM THE PLATINUM GROUP. THESE CATALYSTS MAY BE PLATINUM, PALLADIUM OR RHODIUM. MOST COMMONLY, THE CATALYST IS PALLADIUM OR PLATINUM BECAUSE OF THEIR LOW COST WHEN COMPARED TO THAT OF RHODIUM. THESE METALS ARE SUPPORTED ON ALUMINA WHICH IS CHOSEN BECAUSE OF ITS HIGH-TEMPERATURE STABILITY, STRENGTH, AND LARGE SURFACE AREA PER UNIT WEIGHT. THE CONCENTRATION OF THE PRECIOUS METAL MAY VARY FROM 0.3 TO 1.0 PERCENT BY WEIGHT. THE DENSITY OF ABATEMENT CATALYST IS NOMINALLY 600 KG PER CUBIC METER. ON COMMERCIALY-AVAILABLE CATALYST THE ALUMINA IS COATED WITH A THIN LAYER OF MATERIAL CALLED A SLIP OR WASH COAT. THIS LAYER INCREASES THE SURFACE AREA OF THE SUPPORT OF THE CATALYST CONSIDERABLY AND GIVES THE CATALYST MORE HIGH TEMPERATURE STABILITY. THE PRECIOUS METAL IS DEPOSITED ON THIS SUPPORT AND IS PRESENT AS SMALL CRYSTALLINE SITES.

THERE ARE TWO BASIC FORMS OF THE FINISHED CATALYST; THE FIRST IS A MONOLITH OR "HONEYCOMB". THESE CATALYSTS ARE MADE IN BLOCKS WHICH ARE A RECTANGULAR SHAPE. THE SIZE OF THE BLOCK MAY BE 22.9 CENTIMETERS SQUARE BY 7.6 CENTIMETERS DEEP OR 30.5 CENTIMETERS SQUARE BY 2.5 CENTIMETERS DEEP. THE CATALYST HAS A HONEYCOMB APPEARANCE BECAUSE IT HAS SMALL CHANNELS RUNNING THROUGH IT IN A PARALLEL DIRECTION. THE HONEYCOMB CATALYST CAN BE USED IN REACTORS THAT ARE DESIGNED FOR A SPACE VELOCITY OF 100,000 HR^{-1} . THE SPACE VELOCITY IS DEFINED AS STANDARD CUBIC METER OF TAIL GAS PER HOUR PER CUBIC METER OF CATALYST. THE "HONEYCOMB" CATALYST IS POPULAR FOR TWO REASONS: THEY OFFER A LOWER PRESSURE DROP OR POWER LOSS PER UNIT OF BED DEPTH, AND BECAUSE OF THE HIGH SPACE VELOCITY

THE REACTOR IS RELATIVELY SMALL FOR A GIVEN JOB. THE REACTOR, HOWEVER, CAN BE SUBJECT TO POOR PERFORMANCE DUE TO IMPROPER GAS DISTRIBUTION OR TO INADEQUATE MIXING. SINCE THESE BLOCKS ARE STACKED TO A BED DEPTH OF 46 TO 76 CENTIMETERS, IF POOR MIXING IS PRESENT THE CONFIGURATION OF THE HONEYCOMB STRUCTURE TENDS TO RETARD ANY FURTHER MIXING AS THE GASES PASS THROUGH THE BED.

THE SECOND CATALYST FORM IS PARTICULATES AND THESE ARE TYPICALLY 0.635-CENTIMETER-DIAMETER SPHERES. HISTORICALLY, THE PARTICULATE CATALYST IS MORE RELIABLE AND HAS A LONGER LIFE THAN DOES THE HONEYCOMB CATALYST. BECAUSE IT IS A PACKED BED, THE GAS CAN REDISTRIBUTE IN THE RADIAL DIRECTION, THUS COMPENSATE FOR POOR GAS DISTRIBUTION AND IMPROPER MIXING. THE REACTOR CAN BE DESIGNED IN A LESS CRITICAL FASHION IF A PARTICULATE CATALYST IS USED. SOME OF THE DISADVANTAGES OF PARTICULATE CATALYST: ON A COMPARABLE BASIS THERE IS A HIGHER PRESSURE LOSS PER UNIT BED THICKNESS AND THE REACTOR IS LARGE BECAUSE THE DESIGN SPACE VELOCITY IS APPROXIMATELY 30,000 HR⁻¹.

THE ACTUAL OPERATING KINETICS OF THE CATALYST APPEAR TO CHANGE OVER THE LIFE OF THE CATALYST. WITH FRESH CATALYST, THE RATE-LIMITING STEP IS EXTERNAL MASS TRANSFER. AS THE CATALYST BECOMES DEACTIVATED (EITHER THROUGH CRYSTALLINE SITE AGGLOMERATION, DUE TO EXCESSIVELY HIGH TEMPERATURE, OR POISONING BY TRACE MATERIALS IN THE FEED STREAM), THEN THE CONTROLLING STEP BECOMES THE INTRINSIC KINETICS. THERE IS EVIDENCE THAT AT VERY HIGH TEMPERATURES, THE DISCRETE METAL SITES ACTUALLY MIGRATE OVER THE CATALYST SURFACE AND SEVERAL SITES MAY FUSE INTO A SINGLE SITE. THIS NEW SITE, OF LARGER MASS, HAS A MUCH LOWER SURFACE AREA THAN THAT OF THE SMALLER SITES FROM WHICH IT WAS FORMED.

CALCULATIONS CAN BE MADE TO COMPARE HONEYCOMB CATALYST WITH PARTICULATE CATALYST. THE CALCULATIONS CAN BE REPEATED COMPARING VARIOUS PARTICULATE SIZES WITH VARIOUS "HONEYCOMB" CHANNEL SIZES. THESE CALCULATIONS HAVE BEEN MADE AND RESULTS REFLECTING CALCULATIONS BASED ON COMMERCIAL CATALYSTS ARE SHOWN IN TABLE (2). TWO COMPARISONS ARE MADE: (1) WHERE THE CONTROLLING STEP IS THE INTRINSIC KINETICS, AND (2) WHERE THE CONTROLLING STEP IS MASS TRANSFER. THE COMPARISONS WERE MADE SHOWING THE VOLUME OF HONEYCOMB CATALYST REQUIRED FOR A GIVEN UNIT AS COMPARED TO THE VOLUME OF PARTICULATE CATALYST REQUIRED FOR THE SAME UNIT. ALSO, THE COMPARISON SHOWS THE PRESSURE LOSS FOR THE PARTICULATE CATALYST WHEN COMPARED TO THE PRESSURE LOSS FOR THE HONEYCOMB CATALYST BED.

TABLE 2 COMPARISONS OF COMMERCIAL PARTICULATE AND HONEYCOMB CATALYSTS

<u>SPHERE DIAMETER</u>	<u>CHANNEL DIAMETER</u>	<u>COMPARISON</u>	<u>CONTROLLING STEP</u>	
			<u>INTRINSIC KINETICS</u>	<u>MASS TRANSFER</u>
0.64	0.15	V_H/V_P $\Delta P_P/P_H$	21 1.5	$(1.4)^{-1}$ 44

V_H = VOLUME OF HONEYCOMB CATALYST
 V_P = VOLUME OF PARTICULATE CATALYST
 ΔP_P = PRESSURE DROP THROUGH PARTICULATE CATALYST
 ΔP_H = PRESSURE DROP THROUGH HONEYCOMB CATALYST

IT SHOULD BE NOTED THAT THERE IS A LARGE DIFFERENCE BETWEEN THE EXPECTED PERFORMANCE OF THESE CATALYSTS AND SEVERAL CONCLUSIONS CAN BE DRAWN. (BASED ON CALCULATED DATA NOT SHOWN AS WELL AS DATA SHOWN IN TABLE 2). HONEYCOMB CATALYSTS ARE PREFERRED WHEN THE REACTION IS EXTERNAL MASS TRANSFER CONTROLLED. THE PRESSURE DROP ACROSS THE CATALYST BED IS MUCH LOWER FOR THE HONEYCOMB CATALYST THAN FOR THE PARTICULATE CATALYST. IF THE REACTION IS CONTROLLED BY INTRINSIC KINETICS, THEN THE PARTICULATE CATALYST MAY HAVE A PRESSURE DROP ADVANTAGE. IN GENERAL, HONEYCOMB CATALYST SHOULD BE USED FOR STRONGLY EXOTHERMIC

REACTIONS THAT ARE TO BE RUN ADIABATICALLY. IF THE ACTIVATION ENERGY IS REASONABLY HIGH, THEN THE REACTION WILL BECOME MASS-TRANSFER CONTROLLED AT A POINT VERY CLOSE TO THE INLET SIDE OF THE CATALYST BED.

IF THE REACTION IS CONTROLLED BY INTRINSIC KINETICS, THE USE OF HONEYCOMB CATALYST MAY DEPEND ON A DELICATE PRESSURE-DROP, VOLUME, AND SELECTIVITY TRADEOFF. EVEN THOUGH THE TABLE SHOWS THAT THE REQUIRED VOLUME OF HONEYCOMB CATALYST IS MUCH HIGHER THAN THE REQUIRED VOLUME OF PARTICULATE CATALYST, THE PRESSURE DROP IS USUALLY SMALLER.

CALCULATED DATA SHOWS THAT CHANNEL DIAMETER MAY HAVE AN IMPORTANT INFLUENCE ON HONEYCOMB CATALYST PERFORMANCE. LARGE CHANNEL DIAMETERS ARE PREFERRED FOR KINETICALLY-CONTROLLED REACTIONS. THE USE OF LARGER CHANNEL DIAMETERS RESULTS IN LOWER PRESSURE DROP WITH NO APPRECIABLE CHANGE IN VOLUME REQUIREMENTS. FOR A MASS-TRANSFER CONTROLLED REACTION, SMALL CHANNEL DIAMETERS ARE PREFERRED.

III. EQUIPMENT DESIGN AND ECONOMICS

THE PROPER DESIGN OF THE CATALYTIC ABATEMENT SYSTEM REQUIRES THAT THE SYSTEM NOT ONLY REDUCE THE CONCENTRATION OF ENVIRONMENTALLY OBJECTIONABLE NO_x TO ACCEPTABLE CONCENTRATIONS BUT THE SYSTEM MUST ALSO BE COMPATIBLE WITH NITRIC ACID PLANT OPERATION. THE SYSTEM MUST BE FLEXIBLE TO ALLOW ITS CONTINUED OPERATION DURING MINOR PLANT UPSETS. SINCE THE ABATEMENT REACTIONS ARE EXOTHERMIC AND FUEL IS CONSUMED, THE SYSTEM SHOULD PRODUCE POWER WHICH WILL IMPROVE THE ECONOMICS OF THE ABATEMENT FACILITY.

THE FUNCTION OF THE ABATEMENT EQUIPMENT MUST BE CONSIDERED TO ENSURE THE GOOD PERFORMANCE OF THE SYSTEM. PROVISION MUST BE MADE TO PREHEAT THE TAIL GAS AND INTRODUCE THE FUEL. THE REACTOR MUST BE PROPERLY DESIGNED TO ALLOW THE ABATEMENT REACTION AND PROVISIONS MUST BE INCORPORATED TO EXTRACT AS MUCH OF THE HEAT AS POSSIBLE FOR USEFUL POWER RECOVERY. THE WASTE HEAT IS EXTRACTED BY WASTE-HEAT BOILERS AND POWER-RECOVERY TURBINES.

DECOLORIZERS, WHICH ARE SIMILAR TO ABATEMENT SYSTEMS, HAVE BEEN USED COMMERCIALY SINCE THE MID-1950'S. DEFICIENCIES IN THE DESIGN OF THESE SYSTEMS HAVE SHOWN THAT SEVERAL PROBLEMS CAN BE ENCOUNTERED. ONE OF THESE IS POOR FUEL-TAIL GAS MIXING. AS DISCUSSED EARLIER, THE USE OF HONEYCOMB CATALYST WITH ITS PARALLELLED CHANNELS RUNNING THE FULL LENGTH OF THE CATALYST BED CAN LEAD TO PERFORMANCE LIMITATIONS IF THE FUEL IS NOT ADEQUATELY MIXED WITH THE TAIL GAS. SECONDARILY, IF HYDROCARBON FUELS ARE USED, EXCESSIVE QUANTITIES OF FUEL IN SPECIFIC SEGMENTS OF THE CATALYST BED CAN LEAD TO CRACKING OF THE HYDROCARBON WHICH RESULTS IN CARBON LAYDOWN ON THE CATALYST SURFACE. IMMEDIATELY, THE CATALYST SURFACE BECOMES OCCLUDED BY THE CARBON DEPOSIT AND CAN NO LONGER FUNCTION AS AN ACTIVE CATALYST SITE. IF DURING SHUTDOWN OXYGEN CONCENTRATIONS

BECOME PRESENT IN THE HOT CATALYST BED, THEN EXTREME TEMPERATURES WILL BE REACHED AT THE CATALYST SITE AS THE CARBON BURNS; FUTURE USE OF THE CATALYST WILL BE JEOPARDIZED. REACTION RATE LIMITATIONS MUST ALSO BE CONSIDERED; EXPERIMENTS HAVE SHOWN THAT THE CATALYTIC OXIDATION OF METHANE IS FIRST ORDER IN METHANE AND NEARLY ZERO ORDER IN OXYGEN. (3) THE RATE EQUATION OF THE CATALYTIC REACTION MAY BE EXPRESSED AS FOLLOWS:

$$r = k(C_s)(P_{CH_4})e^{-E/RT} \quad (8)$$

THE C_s REPRESENTS THE SURFACE CONCENTRATION OF THE CATALYST. AS THE CATALYST DEACTIVATES OR AGES, WHICH MAY BE REPRESENTED BY A DECREASE IN C_s , THEN STEPS MUST BE TAKEN TO MAINTAIN THE REACTION RATE. OTHER PARAMETERS MAY BE INCREASED. ONE OF THESE IS THE CONCENTRATION OF THE METHANE. POOR FUEL CONSUMPTION AND AN INCREASE OF THE PROBABILITY OF CARBON DEPOSITION MAY BE THE RESULT. THE SECOND METHOD FOR MAINTAINING THE SAME RATE WITH A DECREASING CATALYST CONCENTRATION IS TO RAISE THE TEMPERATURE OF THE CATALYST BED. THIS IS THE MOST DESIRABLE METHOD BECAUSE IT DOES NOT USE ADDITIONAL FUEL AND DOES NOT JEOPARDIZE THE CATALYST WITH CARBON LAYDOWN WHICH CAN QUICKLY DEACTIVATE THE CATALYST. IT WILL BE NECESSARY TO INCREASE THE PREHEAT TEMPERATURE. THE TEMPERATURE RISE IN THE CATALYST BED IS PRIMARILY A FUNCTION OF THE OXYGEN CONCENTRATION AND THE FUEL THAT IS USED. THE REACTOR IS LIMITED BY A MINIMUM INLET TEMPERATURE OR IGNITION TEMPERATURE AND A MAXIMUM EXHAUST TEMPERATURE. THE MAXIMUM EXHAUST TEMPERATURE IS EITHER SET BY THE CATALYST TEMPERATURE LIMITATIONS OR BY THE EQUIPMENT DOWNSTREAM. PROVISION MUST BE MADE TO ALLOW THE SYSTEM TO FUNCTION WITH VARYING CONCENTRATIONS OF OXYGEN WITHOUT THE RISK OF EXCESSIVE TEMPERATURE OF EITHER THE CATALYST OR THE DOWNSTREAM EQUIPMENT. THERE IS ALWAYS ADEQUATE FUEL TO COMBUST THE OXYGEN AND NITROGEN OXIDES. THE CATA-

LYST IS SUBJECT TO POISONING BY SULFUR, HALOGENS, AND BASIC METALS. THE PALLADIUM CATALYSTS ARE ESPECIALLY SENSITIVE TO SULFUR WHICH IS FREQUENTLY PRESENT IN THE FUEL. IF THE SULFUR CONCENTRATION IN THE FUEL IS MUCH ABOVE 1 PPMV, THEN THE SULFUR MUST BE REMOVED.

THE ABATEMENT SYSTEM MUST HAVE SEVERAL ESSENTIAL CONTROL FEATURES. THESE FEATURES INCLUDE VARIABILITY OF THE PREHEAT TEMPERATURE, CONTROL OF THE PROPER FUEL TO OXYGEN RATIO, AND CONTROL OF THE REACTOR TEMPERATURE. THE TEMPERATURE INLET AND THE POWER RECOVERY TURBINE MUST BE PROTECTED AGAINST OVERTEMPORATING.

THE REMAINDER OF THIS PAPER WILL BE DEVOTED TO THE DISCUSSION OF FOUR POSSIBLE ABATEMENT SYSTEM DESIGNS AND THE ECONOMICS OF A SYSTEM FOR A 500 MTPD PLANT. THE FIRST SYSTEM IS VERY SIMPLE AND IS SHOWN IN FIGURE II. THIS SYSTEM USES A SINGLE CATALYST BED AND HAS THE BASIC CONTROL FEATURES. THE SINGLE STAGE ABATEMENT SYSTEM CAN BE USED WHERE THE TEMPERATURE RISE ACROSS THE CATALYST BED IS LESS THAN THE DIFFERENCE BETWEEN THE MAXIMUM OUTLET TEMPERATURE (GENERALLY AROUND 800°C) AND THE IGNITION TEMPERATURE OF THE FUEL. THE TAIL GAS IS PREHEATED TO THE DESIRED TEMPERATURE AND FUEL IS ADDED. A MIXER IS INSTALLED TO ENSURE PROPER MIXING AND THE STREAM IS FED TO THE REACTOR. THE FUEL FLOW IS CONTROLLED BY FUEL AND OXYGEN ANALYZER/RATIO CONTROL STATION. THIS STATION MONITORS THE FUEL/OXYGEN RATIO TO ENSURE THAT AN EXCESS OF FUEL IS ALWAYS PRESENT. DOWNSTREAM OF THE CATALYST BED THERE IS A TEMPERATURE SENSING POINT WHICH PROVIDES THE INPUT TO A CONTROL STATION WHICH CONTROLS THE PREHEAT TEMPERATURE OR WILL SHUT OFF THE FUEL IF THE MAXIMUM TEMPERATURE IS EXCEEDED. THE WASTE-HEAT BOILER REDUCES THE TEMPERATURE OF THE EXIT STREAM TO A TEMPERATURE THAT IS ACCEPTABLE FOR THE POWER RECOVERY TURBINE.

IN CASES WHERE THE OXYGEN CONCENTRATION OR THE FUEL HEATING VALUE IS SUCH THAT THE TEMPERATURE RISE THAT IS REQUIRED TO ACHIEVE ABATEMENT IS GREATER THAN THAT WHICH CAN BE TOLERATED IN A SINGLE STAGE, THEN A DIFFERENT SYSTEM DESIGN IS REQUIRED. THE FIRST OF THESE EQUIPMENT CONFIGURATIONS IS A TWO-STAGE UNIT WHICH HAS INTERSTAGE COOLING. AGAIN, THE TAIL GAS IS PREHEATED, FUEL IS ADDED AND MIXED. THE FIRST STAGE FUEL IS ADDED SUCH THAT ONLY A PORTION OF THE OXYGEN WILL BE COMBUSTED. THE OXYGEN CONCENTRATION AND SOME OF THE NO₂ IS REDUCED IN THE FIRST STAGE AND IS COOLED BY A WASTE HEAT BOILER. AGAIN, FUEL IS ADDED IN EXCESS AND THE MIXTURE IS FED TO THE SECOND STAGE CATALYST. IN THIS STAGE ABATEMENT IS ACHIEVED. THERE IS A WASTE HEAT BOILER TO EXTRACT HEAT AND TO ALLOW THE EXPANDER TO OPERATE WITHIN ACCEPTABLE TEMPERATURE LIMITS. THIS SYSTEM IS SHOWN IN FIGURE III.

FIGURE IV SHOWS A VARIATION OF THE TWO-STAGE ABATEMENT SYSTEM. HERE THE TAIL GAS IS SPLIT; ONE PORTION GOING THROUGH A PREHEATER. FUEL IS ADDED SIMILARLY TO THE PREVIOUS EXAMPLE AND THE MIXTURE IS FED TO THE FIRST STAGE CATALYST. HERE, AS IN THE SYSTEM DESCRIBED IN FIGURE III, SOME OF THE OXYGEN IS COMBUSTED AND SOME OF THE NO₂ IS REDUCED TO NO. THE OTHER PORTION OF THE TAIL GAS WHICH WAS NOT PREHEATED IS ADDED AT THIS POINT. THIS COLD TAIL GAS COOLS THE EFFLUENT FROM THE FIRST STAGE, MORE FUEL IS ADDED IN EXCESS, AND THE MIXTURE PASSES THROUGH THE SECOND STAGE CATALYST WHERE ABATEMENT IS ACHIEVED. A WASTE HEAT BOILER IS USED TO COOL THE EFFLUENT.

THE TWO DUAL-STAGE SYSTEMS THAT HAVE BEEN DESCRIBED CAN BE DESIGNED FOR REASONABLY HIGH OXYGEN CONCENTRATIONS; HOWEVER, THEY HAVE CERTAIN INHERENT DISADVANTAGES. ONE DISADVANTAGE IS CATALYST REQUIREMENT. THE FIRST CASE WHICH HAS A WASTE HEAT BOILER DOWNSTREAM OF THE FIRST STAGE, THE CATALYST REQUIREMENT

IS TWICE THAT REQUIRED IF THE REACTION COULD BE ACCOMPLISHED IN A SINGLE STAGE. TWO FULL-SIZE REACTORS MUST BE USED AND TWO FULL SIZE WASTE-HEAT BOILERS MUST BE INCORPORATED. THE SECOND DESIGN WHICH IS SHOWN IN FIGURE IV HAS SOME OF THE SAME DISADVANTAGES. IF TWENTY PERCENT OF THE TAIL GAS MUST BY-PASS THE PREHEATER, THEN THE FIRST CATALYST BED WILL CONTAIN .8 OF THE CATALYST REQUIREMENT IF THE REACTIONS COULD BE COMPLETED WITH A SINGLE STAGE. THE SECOND CATALYST BED WILL CONTAIN 100 PERCENT OF THE SINGLE-BED CATALYST REQUIREMENT. THE TOTAL CATALYST REQUIREMENT IS 1.8 TIMES THAT WHICH WOULD BE REQUIRED IF A SINGLE STAGE WERE USED AND THE REACTORS WILL BE LARGER BY FACTOR 1.8. BOTH SYSTEMS, FIGURES III AND IV REQUIRE SEPARATE CONTROLLERS FOR EACH CATALYST STAGE AND AN OVERALL COORDINATING CONTROL LOOP TO ALLOW THE SYSTEM TO FUNCTION AS A SINGLE SYSTEM.

THE RECOGNITION OF THE DISADVANTAGES OF THE DUAL-STAGE SYSTEMS, THE HIGH CAPITAL COST OF THESE SYSTEMS, AND POTENTIAL PROBLEMS THAT MAY BE INHERENTLY PRESENT, HAVE LED TO THE DEVELOPMENT OF A SINGLE-STAGE SYSTEM WITH RECYCLE. THIS SYSTEM IS SHOWN IN FIGURE V. THE TAIL GAS IS PREHEATED AND PASSES THROUGH A RECYCLE EJECTOR. EFFLUENT FROM THE CATALYST BED IS MIXED WITH FRESH TAIL GAS AND THE MIXTURE IS FED TO THE REACTOR. EFFLUENT FROM THE CATALYST BED CONTAINS ESSENTIALLY NO OXYGEN OR NO_x. THE RESULTANT MIXTURE IS ANALYZED AND THE PROPER FUEL FLOW IS SET BY THE ANALYZER STATION. THE MIXTURE THEN PASSES THROUGH THE CATALYST BED WHICH IS A SINGLE STAGE AND THE WASTE RECOVERY EQUIPMENT. THE OXYGEN CONCENTRATION CAN BE MONITORED AND THE RECYCLE RATE VARIED TO COMPENSATE FOR CHANGES IN PLANT OPERATIONS. THE CATALYST BED IS ALWAYS EXPOSED TO THE FULL FUEL CONCENTRATION AND SOME OF THE EXCESS FUEL IS RECYCLED BACK TO THE BED, THUS CONSERVING FUEL. WHEN COMPARING THIS SYSTEM WITH THE TWO DUAL

STAGE SYSTEMS PREVIOUSLY DISCUSSED WHERE 20 PERCENT OF THE GAS WAS USED FOR COOLING PURPOSES, THEN THE CATALYST REQUIREMENT WOULD BE ONLY 1.2 TIMES THAT WHICH WOULD BE REQUIRED FOR A SINGLE STAGE IF ABATEMENT COULD BE COMPLETED WITH NO DILUTION. THIS LEADS TO ECONOMIES IN THE QUANTITY OF CATALYST THAT MUST BE PURCHASED AND REACTOR SIZE. ONLY ONE WASTE HEAT BOILER MUST BE PURCHASED.

TABLE III SHOWS SOME SELECTED COST AND UTILITY REQUIREMENTS THAT ARE PROJECTED FOR A 500 METRIC TON PER DAY PLANT WHICH HAS AN ON-STREAM RATE OF 93%. THE CATALYST LIFE WAS SET AT TWO YEARS WHICH MAY EASILY BE ACHIEVED AND THE PRESENT PRICE OF CATALYST IS ABOUT \$100 PER KILOGRAM. THE NET FUEL REQUIREMENT IS 16.4 STANDARD CUBIC METERS PER TON, IF CREDIT IS GIVEN FOR THE WASTE HEAT STEAM PRODUCED BY THE ABATEMENT SYSTEM. THE PREDOMINANT ECONOMIC BENEFIT OF THE SYSTEM COMES FROM THE POWER RECOVERY OF THE EXPANDER.

TABLE III SELECTED COST AND UTILITY REQUIREMENTS FOR A CATALYTIC ABATEMENT SYSTEM (500 METRIC TON PER DAY PLANT CAPACITY AND 340 DAYS PER YEAR OPERATION)

TOTAL ERECTED COST	=	\$624,900
CATALYST COST (2 YR LIFE)	=	\$0.17 PER TON
FUEL CREDIT FOR STEAM	=	40.2 STANDARD CUBIC METERS PER TON
FUEL REQUIREMENT	=	56.6 STANDARD CUBIC METERS PER TON
POWER RECOVERED IN EXPANDER	=	9,778 kcal PER TON

FIGURE I - RELATIONSHIP OF NITROGEN OXIDES CONCENTRATION AND TEMPERATURE AT REACTOR EXIT. (1)

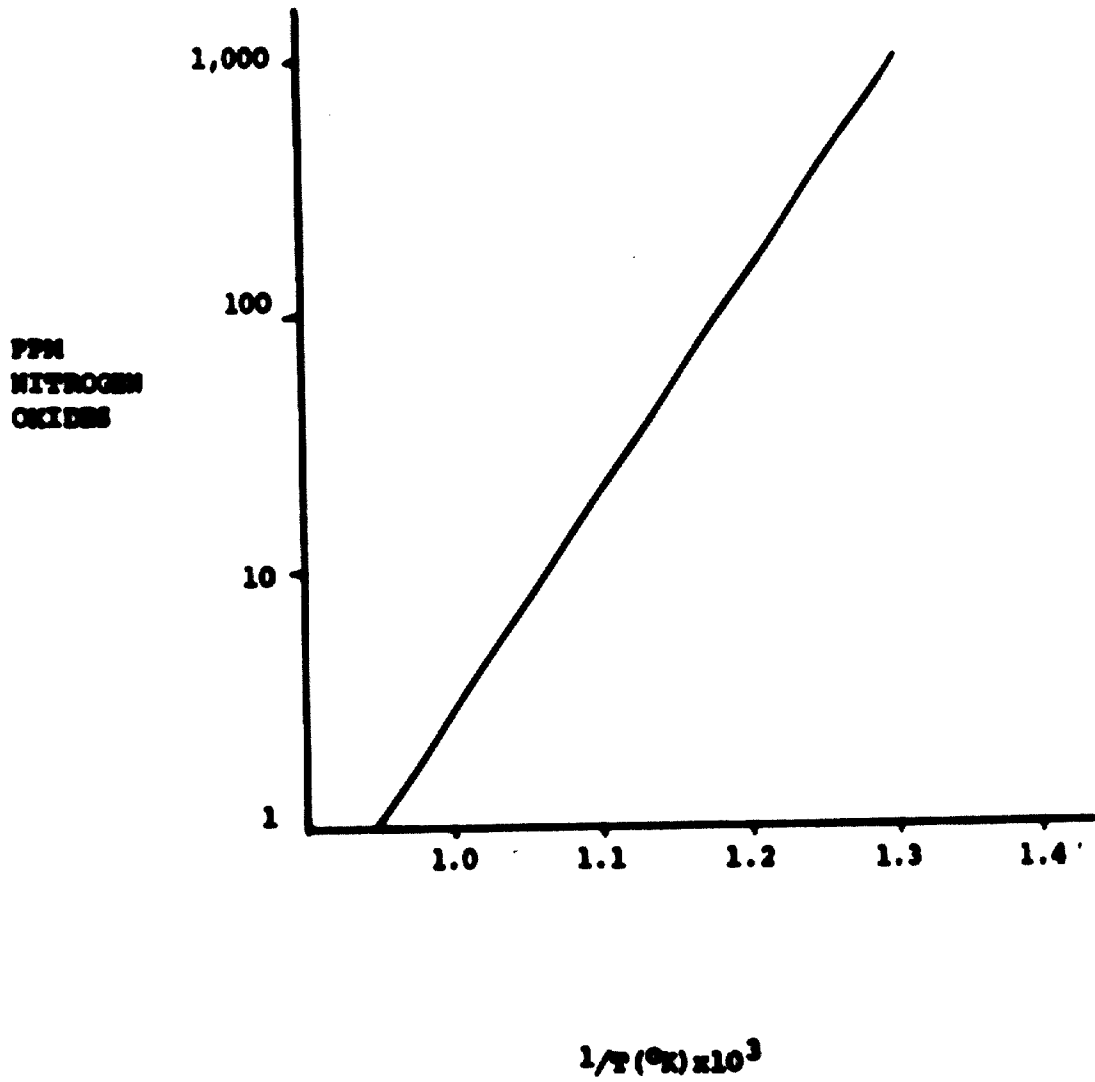


FIGURE II. SINGLE STAGE ABATEMENT SYSTEM

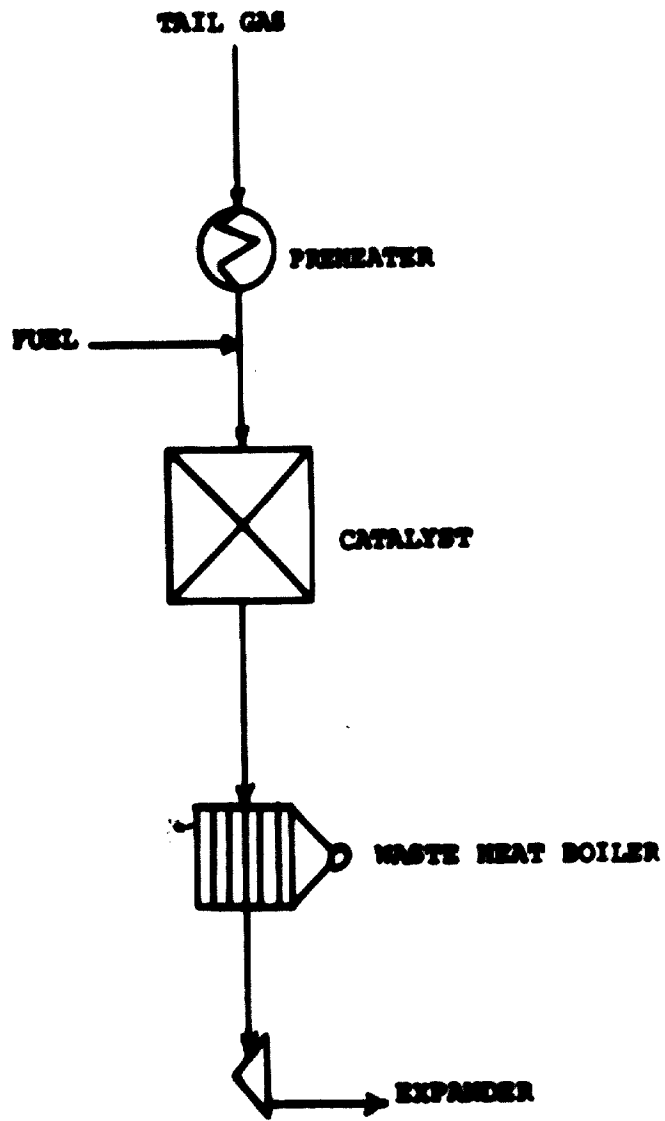


FIGURE III. TWO STAGE ABATEMENT SYSTEM

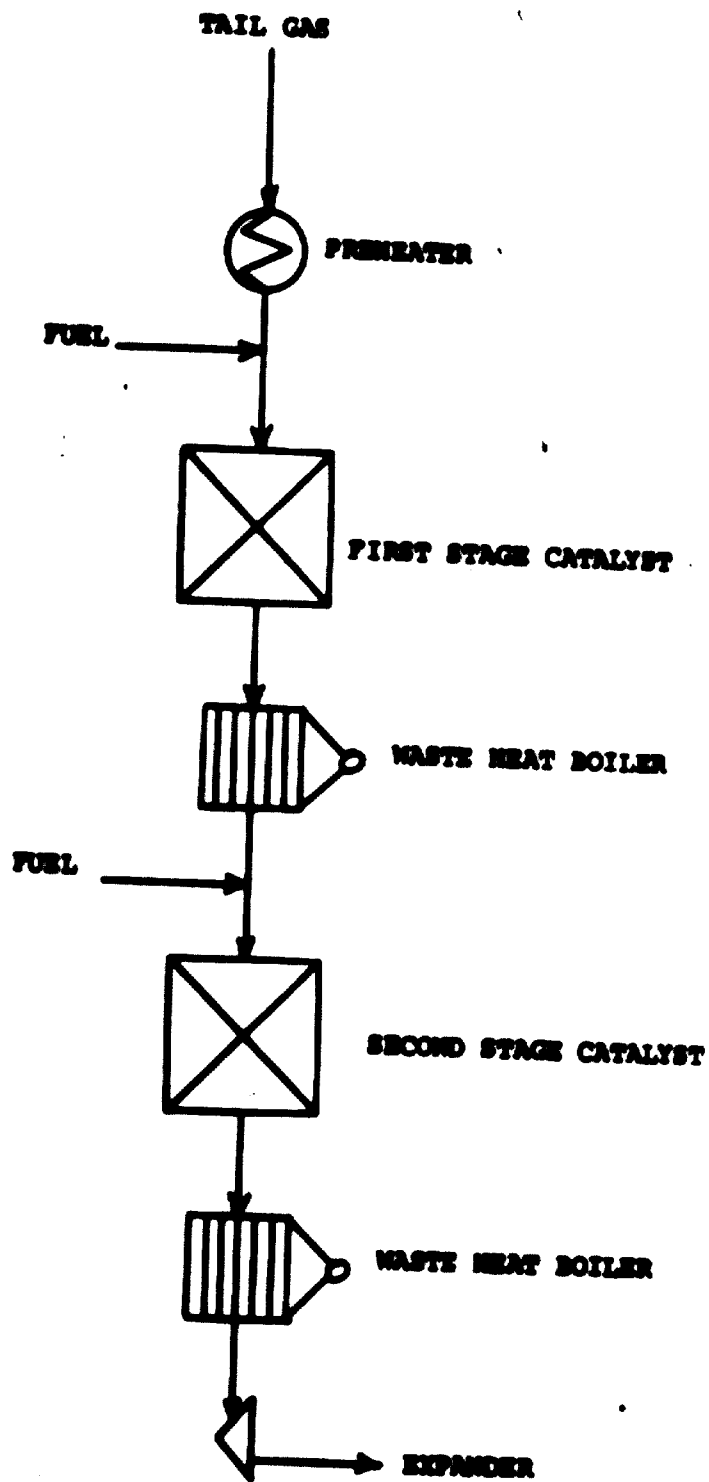


FIGURE IV. TWO STAGE ABATEMENT SYSTEM WITH BYPASS

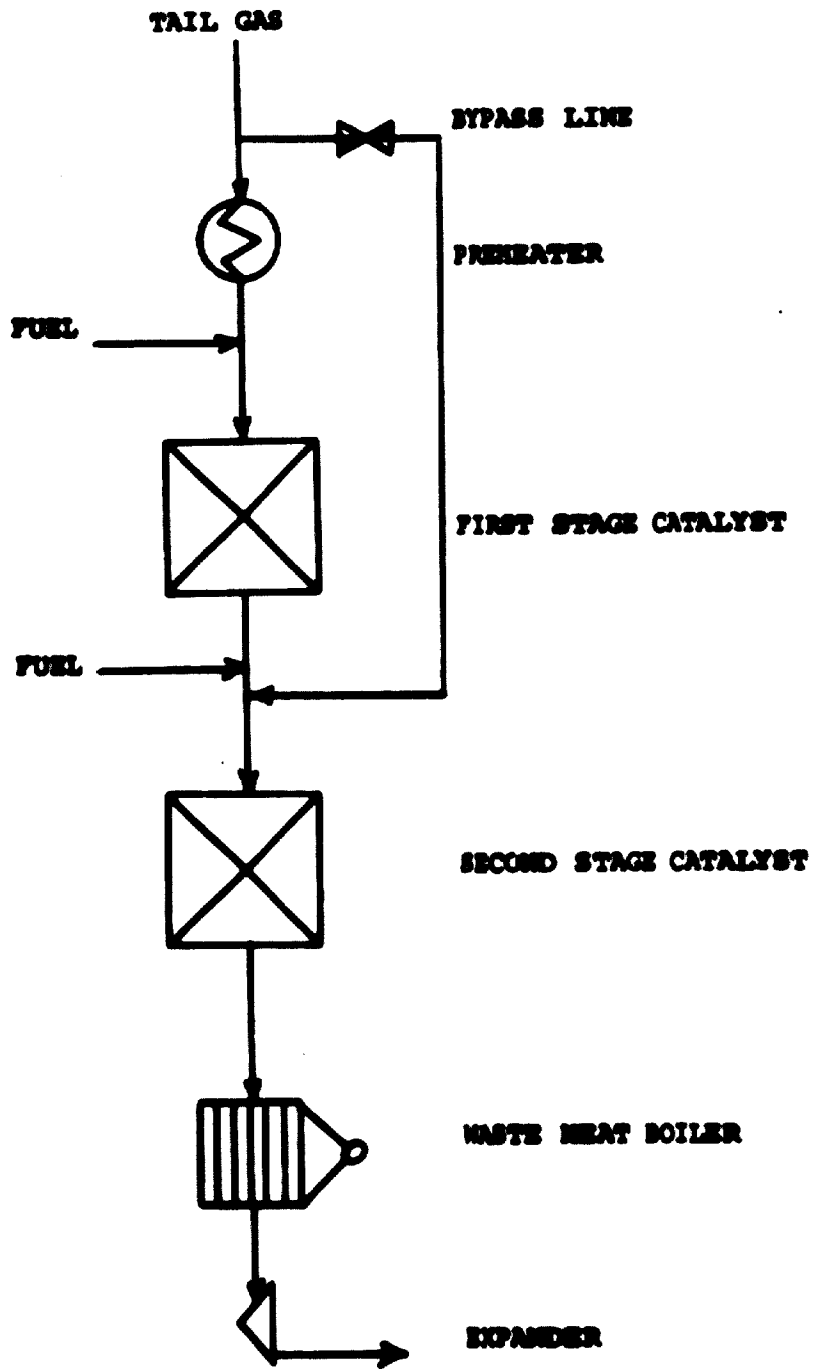
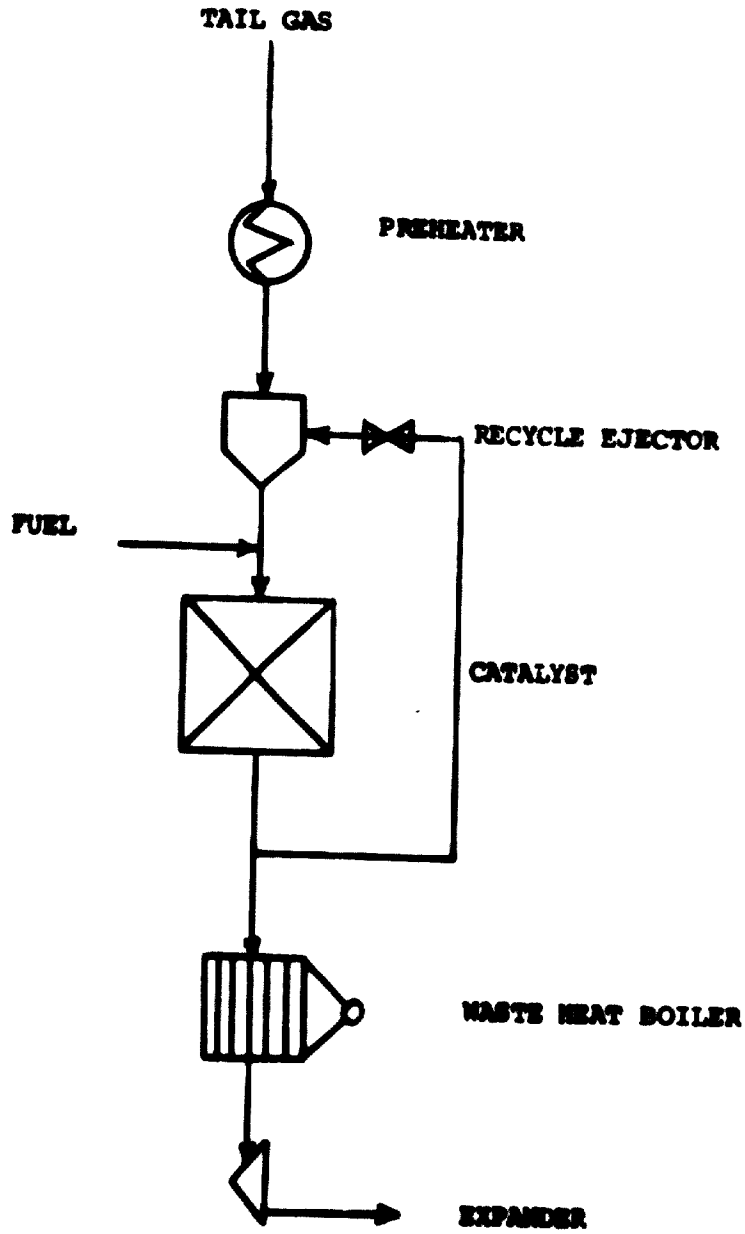
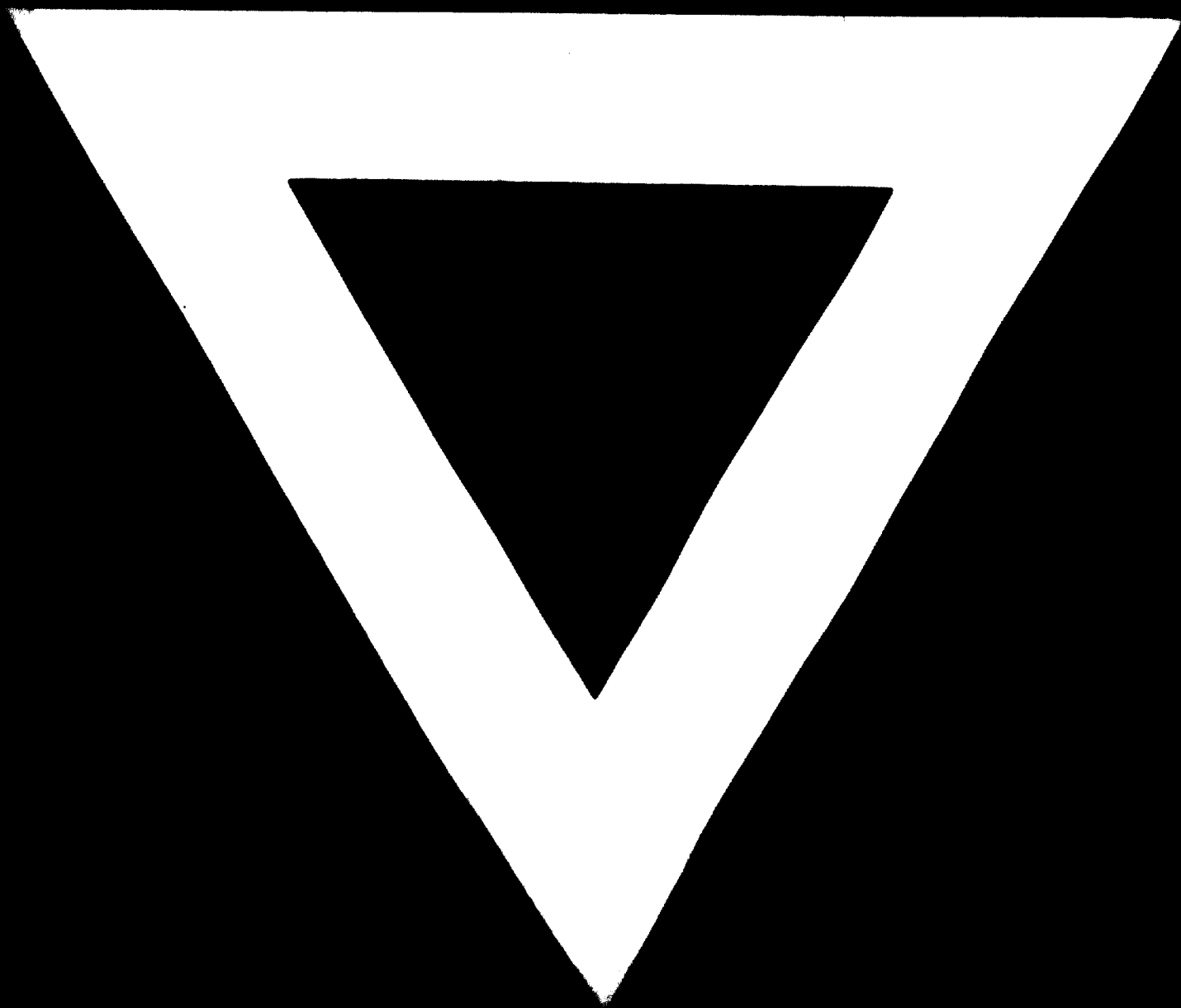


FIGURE V. SINGLE STAGE ABATEMENT SYSTEM WITH RECYCLE



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