

SUOMEN SOODAKATTILAYHDISTYS SUOMEN SUODAKAT HLATHUUSTTS FINNISH RECOVERY BOILER COMMITTEE

**Finnish Recovery Boiler Committee** 

**Recommended procedure for** incineration of non-condensible gases

Original version, May 30, 2002 Revision A, December 16, 2005 Revision B, June 17, 2014

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### PREFACE

This recommendation issued by the Finnish Recovery Boiler Committee is the second updated version of the original recommendation of May 30, 2002. The recommendation has been updated based on the experiences gained in pulp mill projects during the last few years. The updating work started in late 2010 and was finished in the spring of 2013.

Responsible for preparing this revision B has been the working group established by the Finnish Recovery Boiler Committee, with the following members: Marja Heinola and Risto Honkanen of Andritz Oy, Kari Haaga and Tuomo Hilli of Metso Power Oy, Ismo Tapalinen of UPM-Kymmene Kaukas Mill, Lauri Mattila of UPM-Kymmene Oyj Pietarsaari Mill, Raine Rantanen of UPM-Kymmene Kymi Mill, Esa Vakkilainen of Lappeenranta University of Technology and with Markus Nieminen Pöyry Finland Oy as secretary. Group wishes to thank Reijo Hukkanen of Stora Enso Oyj for his numerous expert comments.

Responsible for preparing revision A was the Finnish Recovery Boiler Committee's Environmental Working Group, with Pekka Posti of Oy Metsä-Botnia Ab as chairman, with Sebastian Kankkonen of Jaakko Pöyry Oy as secretary, with Aimo Hakkarainen of Andritz-Ahlstrom Oy, Jouni Hiltunen of Stora Enso Fine Paper Oy, Markku Isoniemi of Kvaerner Pulp Oy, Kari Parviainen of Jaakko Pöyry Oy, Matti Tikka of Kymi Paper Oy, Esko Talka of the Finnish Pulp and Paper Research Institute KCL, and Juha Tolvanen of Alstom Power Finland Oy as members and Esa Vakkilainen of Jaakko Pöyry Oy as expert adviser.

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Finland Oy as members, and with Esa Vakkilainen of Jaakko Pöyry Oy as expert adviser.

The recommendation does not attempt to present a uniform system for handling non-condensible gases nor promote the use of uniform equipment or process designs.

Instead, the recommendation provides basic information for use in engineering, manufacture and operation. As the intention is to develop the recommendation further, we ask you send your possible comments on mistakes, improvement proposals and experiences to the Secretariat of the Finnish Recovery Boiler Committee. Our contact information is found on the Committee's web site: <u>http://www.soodakattilayhdistys.fi</u>.

The Finnish Recovery Boiler Committee assumes no responsibility for errors in this recommendation nor for problems that might arise through use of this document. The possible updated document is available for members on the Committee's web site or thought the Secretariat.

The Finnish Recovery Boiler Committee

# CONTENTS

1	GENERAL	.1
2	DEFINITIONS AND ABBREVIATIONS	.3
2.1	DILUTE NON-CONDENSIBLE GASES (DNCG)	
2.2	DISSOLVING TANK AND MIXING TANK VENT GASES	
2.3	CONCENTRATED NON-CONDENSIBLE GAS (CNCG)	
2.4	HYDROGEN SULPHIDE	
2.5	METHYL MERCAPTAN	
2.6	DIMETHYLE SULPHIDE / DIMETHYLE DISULPHIDE	
2.7	METHANOL	
2.8	TURPENTINE	
2.9	EXPLOSION LIMITS	
2.9.1	EXPLOSION LIMIT FORMULAS	
2.10	ABBREVIATIONS	10
3	IMPACTS ON RECOVERY BOILER EMISSIONS	11
3.1	IMPACTS ON RECOVERY BOILER SULPHUR EMISSIONS	11
3.2	IMPACTS ON RECOVERY BOILER TRS EMISSIONS	
3.3	IMPACTS ON RECOVERY BOILER FOULING	
3.4	IMPACTS ON RECOVERY BOILER NO <sub>X</sub> EMISSIONS	
3.4.1	IMPACT OF DNCG	
3.4.2	IMPACT OF DISSOLVING TANK VENT GASES	13
3.4.3	IMPACT OF CNCG	14
3.4.4	IMPACT OF METHANOL	14
3.5	IMPACTS ON OTHER RECOVERY BOILER FUNCTIONS	15
4	RISKS AND CORROSION RELATED TO NCG SYSTEMS	16
4.1	LEAKAGE OF NON-CONDENSIBLE GASES INTO MANNED AREAS	16
4.1.1	Odour	
4.1.2	SAFETY EQUIPMENT	17
4.2	CONDENSATE DRAINING PROBLEMS	17
4.2.1	OVERFLOWING OF CONDENSATE TRAP	18
4.2.2	DRYING OUT OF WATER SEALS	18
4.2.3	PLUGGING OF WATER SEALS	18
4.3	EXPLOSION RISKS IN NCG LINES	18
4.3.1	SHUT-DOWN AND START-UP SITUATIONS	19
4.4	GAS EXPLOSION IN BOILER	
4.5	SMELT-WATER EXPLOSION IN BOILER	40
4.6		
	CORROSION PROBLEMS	19
4.7		19
	CORROSION PROBLEMS	19 20
4.7	CORROSION PROBLEMS SPARKING / STATIC ELECTRICITY	19 20 21
4.7 5	CORROSION PROBLEMS SPARKING / STATIC ELECTRICITY DNCG SYSTEMS IN A RECOVERY BOILER	19 20 21 21
4.7 5 5.1	CORROSION PROBLEMS SPARKING / STATIC ELECTRICITY DNCG SYSTEMS IN A RECOVERY BOILER COMPOSITION AND AMOUNT	19 20 21 21 23
4.7 5 5.1 5.2	CORROSION PROBLEMS SPARKING / STATIC ELECTRICITY DNCG SYSTEMS IN A RECOVERY BOILER COMPOSITION AND AMOUNT COOLING / HEATING	19 20 21 21 23 23

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5.3.2	TRIPPING LOGIC FOR INTRODUCING DNCG	26
5.4	DUCTS	26
5.4.1	FLOW	26
5.4.2	POTENTIAL BALANCING	26
5.5	VALVES / DAMPERS	27
5.6	FAN	27
5.7	Make-up air inlet	27
5.8	SCRUBBERS / CONDENSERS	27
5.9	DROPLET SEPARATOR	28
5.10	CONDENSATE DRAINING	28
5.10.1	SIZE OF CONDENSATE DRAIN LINES	28
5.10.2	DUCT SLOPES AND LOCATIONS OF CONDENSATE DRAINS	28
5.10.3	WATER SEALS	29
5.11	FLAME ARRESTER	29
5.12	BYPASS	29
5.13	UNDERPRESSURE PROTECTION DEVICE	29
5.14	<b>OVERPRESSURE PROTECTION DEVICE</b>	29
5.14.1	RUPTURE DISC	
5.15	CONCENTRATION MEASUREMENT	30
6	DISSOLVING TANK VENT GAS SYSTEMS AT THE RECOVERY BOILER	31
6.1	COMPOSITION AND AMOUNT	31
6.2	MIXING TANK VENT GASES	32
6.3	COOLING / HEATING	32
6.4	STARTING / TRIPPING LOGIC FOR THE INCINERATION OF VENT GASES	32
6.4.1	STARTING LOGIC FOR INTRODUCING DISSOLVING TANK VENT GASES	33
6.4.2	TRIPPING LOGIC FOR INTRODUCING DISSOLVING TANK VENT GASES	33
6.5	DUCTS	34
6.5.1	FLOW	34
6.5.2	POTENTIAL BALANCING	34
6.6	VALVES / DAMPERS	34
6.7	FAN	35
6.8	SCRUBBER	35
6.9	DROPLET SEPARATOR	35
6.10	WASHING OF DROPLET SEPARATOR AND VENT GAS HEATER	35
6.11	CONDENSATE DRAINING	35
6.11.1	SIZE OF CONDENSATE DRAINS	36
6.11.2	DUCT SLOPES AND LOCATIONS OF CONDENSATE DRAINS	36
6.11.3	WATER SEALS	36
6.12	FLAME ARRESTER	36
6.13	BYPASS	37
6.14	OVERPRESSURE PROTECTION	37
6.14.1	RUPTURE DISC	37
6.15	CONCENTRATION MEASUREMENT	37
_		
7	INCINERATION OF CNCG IN THE RECOVERY BOILER	
7.1	COMPOSITION AND AMOUNT	
7.2	STARTING / TRIPPING LOGIC FOR INCINERATION OF CNCG	40

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#### RECOMMENDED PROCEDURE FOR INCINERATION OF NON-CONDENSIBLE GASES

7.2.1	STARTING LOGIC FOR THE CNCG INCINERATION	41
7.2.2	TRIPPING LOGIC FOR THE CNCG INCINERATION	41
7.2.3	CAPACITY LIMIT	42
7.2.4	BURNER AND USE OF SUPPORT FLAME	42
7.3	PIPELINE SYSTEM	
7.3.1	STEAM PURGING OF PIPELINES	44
7.3.2	PIPELINE PRESSURE MEASUREMENTS	45
7.3.3	POTENTIAL BALANCING	45
7.4	TRANSFER OF CNCG	45
7.4.1	PRESSURE-CONTROL STEAM	46
7.4.2	VALVES	46
7.4.3	HEATING/COOLING	46
7.4.4	DROPLET SEPARATOR	46
7.4.5	FLAME ARRESTER	47
7.4.6	UNDERPRESSURE PROTECTION	47
7.4.7	OVERPRESSURE PROTECTION	47
7.4.8	RUPTURE DISCS	47
7.5	CONDENSATE DRAINING	48
7.5.1	SIZE OF CONDENSATE DRAINING LINES	48
7.5.2	PIPE SLOPES AND LOCATIONS OF CONDENSATE DRAINS	48
7.5.3	WATER SEALS	49
7.6	ALTERNATIVE LOCATION	49
7.6.1	STEAM PURGING	49
7.6.2	LOCATION OF FLARE	50
7.7	CONCENTRATION MEASUREMENT	50
8	METHANOL / TURPENTINE INCINERATION IN THE RECOVERY BOILE	R51
8 8.1	METHANOL / TURPENTINE INCINERATION IN THE RECOVERY BOILE Starting / tripping logic of the methanol/turpentine incineration	R51 51
<b>8</b> <b>8.1</b> 8.1.1	METHANOL / TURPENTINE INCINERATION IN THE RECOVERY BOILE STARTING / TRIPPING LOGIC OF THE METHANOL/TURPENTINE INCINERATION STARTING LOGIC FOR METHANOL AND TURPENTINE BURNING	<b>R51</b> 51 52
<b>8</b> <b>8.1</b> 8.1.1 8.1.2	METHANOL / TURPENTINE INCINERATION IN THE RECOVERY BOILE STARTING / TRIPPING LOGIC OF THE METHANOL/TURPENTINE INCINERATION STARTING LOGIC FOR METHANOL AND TURPENTINE BURNING TRIPPING LOGIC FOR METHANOL AND TURPENTINE INCINERATION	<b>R51</b> 51 52 52
<b>8</b> <b>8.1</b> 8.1.1 8.1.2 <b>8.2</b>	METHANOL / TURPENTINE INCINERATION IN THE RECOVERY BOILE STARTING / TRIPPING LOGIC OF THE METHANOL/TURPENTINE INCINERATION STARTING LOGIC FOR METHANOL AND TURPENTINE BURNING TRIPPING LOGIC FOR METHANOL AND TURPENTINE INCINERATION ELECTRICAL AND AUTOMATION SYSTEMS OF THE BURNER	<b>R51</b> 51 52 52 53
<b>8</b> <b>8.1</b> 8.1.1 8.1.2	METHANOL / TURPENTINE INCINERATION IN THE RECOVERY BOILE STARTING / TRIPPING LOGIC OF THE METHANOL/TURPENTINE INCINERATION STARTING LOGIC FOR METHANOL AND TURPENTINE BURNING TRIPPING LOGIC FOR METHANOL AND TURPENTINE INCINERATION	<b>R51</b> 51 52 52 53
<b>8</b> <b>8.1</b> 8.1.1 8.1.2 <b>8.2</b>	METHANOL / TURPENTINE INCINERATION IN THE RECOVERY BOILE STARTING / TRIPPING LOGIC OF THE METHANOL/TURPENTINE INCINERATION STARTING LOGIC FOR METHANOL AND TURPENTINE BURNING TRIPPING LOGIC FOR METHANOL AND TURPENTINE INCINERATION ELECTRICAL AND AUTOMATION SYSTEMS OF THE BURNER VALVES	<b>R51</b> <b>51</b> 52 52 <b>53</b> <b>53</b>
<ul> <li>8</li> <li>8.1</li> <li>8.1.1</li> <li>8.1.2</li> <li>8.2</li> <li>8.3</li> <li>9</li> </ul>	METHANOL / TURPENTINE INCINERATION IN THE RECOVERY BOILE STARTING / TRIPPING LOGIC OF THE METHANOL/TURPENTINE INCINERATION STARTING LOGIC FOR METHANOL AND TURPENTINE BURNING TRIPPING LOGIC FOR METHANOL AND TURPENTINE INCINERATION ELECTRICAL AND AUTOMATION SYSTEMS OF THE BURNER VALVES	<b>R51</b> 51 52 53 53 53
8 8.1 8.1.1 8.1.2 8.2 8.3 9 9.1	METHANOL / TURPENTINE INCINERATION IN THE RECOVERY BOILE STARTING / TRIPPING LOGIC OF THE METHANOL/TURPENTINE INCINERATION STARTING LOGIC FOR METHANOL AND TURPENTINE BURNING TRIPPING LOGIC FOR METHANOL AND TURPENTINE INCINERATION ELECTRICAL AND AUTOMATION SYSTEMS OF THE BURNER VALVES ACTIONS IN SPECIAL SITUATIONS	<b>R51</b> <b>51</b> 52 52 <b>53</b> <b>53</b> <b>54</b> <b>54</b>
8 8.1 8.1.1 8.1.2 8.2 8.3 9 9.1 9.2	METHANOL / TURPENTINE INCINERATION IN THE RECOVERY BOILE STARTING / TRIPPING LOGIC OF THE METHANOL/TURPENTINE INCINERATION STARTING LOGIC FOR METHANOL AND TURPENTINE BURNING TRIPPING LOGIC FOR METHANOL AND TURPENTINE INCINERATION ELECTRICAL AND AUTOMATION SYSTEMS OF THE BURNER VALVES ACTIONS IN SPECIAL SITUATIONS ACTIONS DURING DISTURBANCES ACTIONS DURING SHUT-DOWNS	<b>R51</b> 51 52 52 53 53 54 54 54
8 8.1 8.1.1 8.1.2 8.2 8.3 9 9.1 9.2 9.3	METHANOL / TURPENTINE INCINERATION IN THE RECOVERY BOILE STARTING / TRIPPING LOGIC OF THE METHANOL/TURPENTINE INCINERATION STARTING LOGIC FOR METHANOL AND TURPENTINE BURNING TRIPPING LOGIC FOR METHANOL AND TURPENTINE INCINERATION ELECTRICAL AND AUTOMATION SYSTEMS OF THE BURNER VALVES ACTIONS IN SPECIAL SITUATIONS ACTIONS DURING DISTURBANCES ACTIONS DURING SHUT-DOWNS ACTIONS DURING START-UPS	<b>R51</b> 51 52 53 53 54 54 54 54
8 8.1 8.1.1 8.1.2 8.2 8.3 9 9.1 9.2 9.3 9.4	METHANOL / TURPENTINE INCINERATION IN THE RECOVERY BOILE STARTING / TRIPPING LOGIC OF THE METHANOL/TURPENTINE INCINERATION STARTING LOGIC FOR METHANOL AND TURPENTINE BURNING TRIPPING LOGIC FOR METHANOL AND TURPENTINE INCINERATION ELECTRICAL AND AUTOMATION SYSTEMS OF THE BURNER VALVES ACTIONS IN SPECIAL SITUATIONS ACTIONS DURING DISTURBANCES ACTIONS DURING START-UPS ACTIONS DURING START-UPS	<b>R51</b> 52 52 53 53 54 54 54 54 54
8 8.1 8.1.1 8.1.2 8.2 8.3 9 9.1 9.2 9.3	METHANOL / TURPENTINE INCINERATION IN THE RECOVERY BOILE STARTING / TRIPPING LOGIC OF THE METHANOL/TURPENTINE INCINERATION STARTING LOGIC FOR METHANOL AND TURPENTINE BURNING TRIPPING LOGIC FOR METHANOL AND TURPENTINE INCINERATION ELECTRICAL AND AUTOMATION SYSTEMS OF THE BURNER VALVES ACTIONS IN SPECIAL SITUATIONS ACTIONS DURING DISTURBANCES ACTIONS DURING SHUT-DOWNS ACTIONS DURING START-UPS	<b>R51</b> 52 52 53 53 54 54 54 55 55
<ul> <li>8</li> <li>8.1</li> <li>8.1.1</li> <li>8.1.2</li> <li>8.2</li> <li>8.3</li> <li>9</li> <li>9.1</li> <li>9.2</li> <li>9.3</li> <li>9.4</li> <li>9.4.1</li> <li>9.4.2</li> </ul>	METHANOL / TURPENTINE INCINERATION IN THE RECOVERY BOILE STARTING / TRIPPING LOGIC OF THE METHANOL/TURPENTINE INCINERATION	<b>R51</b> 52 52 53 53 54 54 54 55 55 56
<ul> <li>8</li> <li>8.1</li> <li>8.1.1</li> <li>8.1.2</li> <li>8.2</li> <li>8.3</li> <li>9</li> <li>9.1</li> <li>9.2</li> <li>9.3</li> <li>9.4</li> <li>9.4.1</li> <li>9.4.2</li> <li>10</li> </ul>	METHANOL / TURPENTINE INCINERATION IN THE RECOVERY BOILE STARTING / TRIPPING LOGIC OF THE METHANOL/TURPENTINE INCINERATION	<b>R51</b> 52 52 53 53 54 54 54 55 55 56 57
<ul> <li>8</li> <li>8.1</li> <li>8.1.1</li> <li>8.1.2</li> <li>8.2</li> <li>8.3</li> <li>9</li> <li>9.1</li> <li>9.2</li> <li>9.3</li> <li>9.4</li> <li>9.4.1</li> <li>9.4.2</li> <li>10</li> <li>10.1</li> </ul>	METHANOL / TURPENTINE INCINERATION IN THE RECOVERY BOILE STARTING / TRIPPING LOGIC OF THE METHANOL/TURPENTINE INCINERATION	<b>R51</b> 52 52 53 53 54 54 54 55 55 55 57 57
<ul> <li>8</li> <li>8.1</li> <li>8.1.1</li> <li>8.1.2</li> <li>8.2</li> <li>8.3</li> <li>9</li> <li>9.1</li> <li>9.2</li> <li>9.3</li> <li>9.4</li> <li>9.4.1</li> <li>9.4.2</li> <li>10</li> <li>10.1</li> <li>10.2</li> </ul>	METHANOL / TURPENTINE INCINERATION IN THE RECOVERY BOILE STARTING / TRIPPING LOGIC OF THE METHANOL/TURPENTINE INCINERATION	<b>R51</b> 52 52 53 53 54 54 54 55 55 56 57 57 57
<ul> <li>8</li> <li>8.1</li> <li>8.1.1</li> <li>8.1.2</li> <li>8.2</li> <li>8.3</li> <li>9</li> <li>9.1</li> <li>9.2</li> <li>9.3</li> <li>9.4</li> <li>9.4.1</li> <li>9.4.2</li> <li>10</li> <li>10.1</li> <li>10.2</li> <li>10.3</li> </ul>	METHANOL / TURPENTINE INCINERATION IN THE RECOVERY BOILE         STARTING / TRIPPING LOGIC OF THE METHANOL/TURPENTINE INCINERATION	<b>R51</b> 52 52 53 53 53 54 54 54 55 55 56 57 57 58
<ul> <li>8</li> <li>8.1</li> <li>8.1.1</li> <li>8.1.2</li> <li>8.2</li> <li>8.3</li> <li>9</li> <li>9.1</li> <li>9.2</li> <li>9.3</li> <li>9.4</li> <li>9.4.1</li> <li>9.4.2</li> <li>10</li> <li>10.1</li> <li>10.2</li> <li>10.3</li> <li>10.4</li> </ul>	METHANOL / TURPENTINE INCINERATION IN THE RECOVERY BOILE STARTING / TRIPPING LOGIC OF THE METHANOL/TURPENTINE INCINERATION	<b>R51</b> 52 52 53 53 53 54 54 55 55 55 57 57 58 58
<ul> <li>8</li> <li>8.1</li> <li>8.1.1</li> <li>8.1.2</li> <li>8.2</li> <li>8.3</li> <li>9</li> <li>9.1</li> <li>9.2</li> <li>9.3</li> <li>9.4</li> <li>9.4.1</li> <li>9.4.2</li> <li>10</li> <li>10.1</li> <li>10.2</li> <li>10.3</li> </ul>	METHANOL / TURPENTINE INCINERATION IN THE RECOVERY BOILE         STARTING / TRIPPING LOGIC OF THE METHANOL/TURPENTINE INCINERATION	<b>R51</b> 52 52 53 53 54 54 54 55 55 55 57 57 57 58 58 58

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10.7	VALVES / DAMPERS		59
10.8	FLANGES, CONNECTION	۶۶	59
10.9	FANS		59
10.10	<b>EJECTORS / LIQUID RIN</b>	G COMPRESSOR	60
10.11	DUCT / PIPE SIZING		60
10.12	LOCATION OF FLAME A	RRESTER	60
10.13	LOCATION OF RUPTUR	E DISCS	61
10.14	LOCATION OF BYPASS.		61
10.15	HAZARDOUS AREA CLA	SSIFICATION	61
10.16	MANUFACTURING PERI	/IITS	62
11	OTHER INSTRUCTI	ONS AND REGULATIONS AFFECTING DESIGN	63
11.1	FINNISH LAW		63
11.1.1		ITY STUDY (HAZOP)	
		LINES	
11.1.3	CLASSIFICATION OF POT	ENTIALLY EXPLOSIVE ATMOSPHERES (ATEX)	64
11.2			
11.3		NS	
11.3.1	SODAHUSKOMMITTÉN		65
11.3.2	BLRBAC		65
12	<b>DEVIATIONS FROM</b>	PRACTICES DESCRIBED IN OTHER INSTRUCTION	IS 66
12 12.1		PRACTICES DESCRIBED IN OTHER INSTRUCTION d to BLRBAC'S instructions	
	<b>DEVIATIONS COMPARE</b>		66
12.1 13	DEVIATIONS COMPARE	D TO BLRBAC'S INSTRUCTIONS	66 67
12.1 13 13.1	DEVIATIONS COMPARE EXAMPLES OF ACC EXAMPLE 1:	D TO BLRBAC'S INSTRUCTIONS	66 67 67
12.1 13 13.1 13.2	DEVIATIONS COMPARE EXAMPLES OF ACC EXAMPLE 1: EXAMPLE 2:	D TO BLRBAC'S INSTRUCTIONS	66 67 67 69
12.1 13 13.1 13.2 13.3	DEVIATIONS COMPARE EXAMPLES OF ACC EXAMPLE 1: EXAMPLE 2: EXAMPLE 3:	D TO BLRBAC'S INSTRUCTIONS	66 67 67 69 70
12.1 13 13.1 13.2	DEVIATIONS COMPARE EXAMPLES OF ACC EXAMPLE 1: EXAMPLE 2: EXAMPLE 3: EXAMPLE 4:	D TO BLRBAC'S INSTRUCTIONS	66 67 67 69 70 71
12.1 13 13.1 13.2 13.3 13.4	DEVIATIONS COMPARE EXAMPLES OF ACC EXAMPLE 1: EXAMPLE 2: EXAMPLE 3: EXAMPLE 4: EXAMPLE 5:	D TO BLRBAC'S INSTRUCTIONS	66 67 67 69 70 71 72
12.1 13 13.1 13.2 13.3 13.4 13.5	DEVIATIONS COMPARE EXAMPLES OF ACC EXAMPLE 1: EXAMPLE 2: EXAMPLE 3: EXAMPLE 4: EXAMPLE 5: EXAMPLE 6:	D TO BLRBAC'S INSTRUCTIONS	66 67 67 70 71 72 74
12.1 13 13.1 13.2 13.3 13.4 13.5 13.6	DEVIATIONS COMPARE EXAMPLES OF ACC EXAMPLE 1: EXAMPLE 2: EXAMPLE 3: EXAMPLE 4: EXAMPLE 5: EXAMPLE 6: EXAMPLE 7:	D TO BLRBAC'S INSTRUCTIONS	66 67 67 70 71 72 74 75
12.1 13 13.1 13.2 13.3 13.4 13.5 13.6 13.7	DEVIATIONS COMPARE EXAMPLES OF ACC EXAMPLE 1: EXAMPLE 2: EXAMPLE 3: EXAMPLE 4: EXAMPLE 5: EXAMPLE 6: EXAMPLE 7: EXAMPLE 8:	D TO BLRBAC'S INSTRUCTIONS	66 67 67 70 71 72 74 75 75
12.1 13 13.1 13.2 13.3 13.4 13.5 13.6 13.7 13.8	DEVIATIONS COMPARE EXAMPLES OF ACC EXAMPLE 1: EXAMPLE 2: EXAMPLE 3: EXAMPLE 4: EXAMPLE 5: EXAMPLE 6: EXAMPLE 6: EXAMPLE 8: EXAMPLE 9:	D TO BLRBAC'S INSTRUCTIONS	66 67 67 70 71 72 74 75 75 76
12.1 13 13.1 13.2 13.3 13.4 13.5 13.6 13.7 13.8 13.9	DEVIATIONS COMPARE EXAMPLES OF ACC EXAMPLE 1: EXAMPLE 2: EXAMPLE 3: EXAMPLE 4: EXAMPLE 5: EXAMPLE 6: EXAMPLE 6: EXAMPLE 8: EXAMPLE 8: EXAMPLE 9:	D TO BLRBAC'S INSTRUCTIONS	66 67 67 70 71 72 74 75 75 76
12.1 13 13.1 13.2 13.3 13.4 13.5 13.6 13.7 13.8 13.9 14 15	DEVIATIONS COMPARE EXAMPLES OF ACC EXAMPLE 1: EXAMPLE 2: EXAMPLE 3: EXAMPLE 4: EXAMPLE 5: EXAMPLE 6: EXAMPLE 6: EXAMPLE 8: EXAMPLE 8: EXAMPLE 9:	D TO BLRBAC'S INSTRUCTIONS	66 67 67 70 71 72 74 75 75 76
12.1 13 13.1 13.2 13.3 13.4 13.5 13.6 13.7 13.8 13.9 14 15	DEVIATIONS COMPARE EXAMPLES OF ACC EXAMPLE 1: EXAMPLE 2: EXAMPLE 3: EXAMPLE 4: EXAMPLE 4: EXAMPLE 5: EXAMPLE 6: EXAMPLE 6: EXAMPLE 8: EXAMPLE 8: EXAMPLE 9: CLOSING WORDS REFERENCES	D TO BLRBAC'S INSTRUCTIONS	66 67 67 70 71 72 74 75 75 76

Appendix III Balance curve: Methanol

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#### 1 GENERAL

Incineration of non-condensible gases (NCG) in recovery boilers is a common procedure. The Finnish Recovery Boiler Committee does not recommend on where NCG should be incinerated. Incineration of NCG in the recovery boiler means an added risk to boiler operation and the handling of NCG may cause safety problems. However, since NCG are nevertheless being incinerated, the members of the committee have called for a clear instruction for the handling of non-condensible pulp mill gases and their incineration in recovery boilers. The Finnish Recovery Boiler Committee wants to improve safety and the performance of the overall process.

This recommendation refers to NCG systems of recovery boilers and related equipment. The recommendation does not express a view as to where and how NCG should be collected or on the equipment related to these functions. A focused approach should be used when designing NCG collection systems. Also, the recommendation does not attempt to present a uniform system for handling NCG, nor promote the use of uniform equipment or process designs. Instead, the recommendation provides basic information for use in engineering, manufacture and operation.

The recovery boiler as an operating environment requires highly reliable and safe systems. It makes good sense to invest in quality equipment and in correct usage. Even very short operating shut-downs caused by disturbances often cost more than the investment required to prevent them. The incineration of NCG makes the recovery boiler operation more complicated, and the handling of inflammable toxic gases increases the risk of accidents. Complying with the instructions in this recommendation will help minimise hazards and dangerous situations.

This recommendation does not express a view on the contents of operator training required for operating NCG collection and incineration systems. Appropriate training programmes are vital before new equipment is taken into use and before new operators are allowed to take control over NCG incineration systems.

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The recommendation does not give guidelines to the mechanical service and maintenance functions of equipment related to NCG systems, but it does express a view on inspection intervals and methods.

In drawing up this recommendation, special care has been taken to confirm careful preparation, while taking into account the opinions of pulp mill operators, equipment suppliers and insurance companies concerning incineration of NCG. This recommendation is based on the assumption that the equipment of a NCG system primarily meets the requirements imposed by the current national laws, regulations and supervisory authorities, including work safety legislation and laws and regulations concerning inflammable liquids and gases. The equipment of NCG systems is also assumed to be professionally designed, first-class, functional and reliable in use and manufactured with top-quality materials and workmanship.

The responsibility for the performance and process design solutions of NCG systems remains with the equipment suppliers. The responsibility for correct and careful operation of NCG systems rests with the operators of the plant. The Finnish Recovery Boiler Committee's recommendation is that the supplier and ultimate user of the plant together perform a hazard and operability study (e.g. HAZOP) of the installation and review the information required by risk assessment. In its report series, the Finnish Recovery Boiler Committee has published report No. 11/2001 entitled "Recovery boiler risk assessment" (in Finnish).

In spite of what is said in this instruction, precedence shall always be given to current laws and regulations and to instructions and guidelines issued by the authorities.

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## 2 DEFINITIONS AND ABBREVIATIONS

Non-condensible gases released during cooking, black liquor handling and causticising, that is hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl disulphide, methanol and turpentine, are inflammable, explosive and strongly odorous compounds giving NCG their characteristic smell. The volatile compounds from wood, in other words turpentine and methanol, are not odorous in a pure state, but in pulp mills they contain impurities in the form of odorous components.

In this recommendation, odorous gases are generally divided into the following categories:

- dilute non-condensible gases (DNCG)
- dissolving and mixing tank vent gases
- concentrated non-condensible gases (CNCG)
- liquid methanol
- liquid turpentine

#### 2.1 Dilute non-condensible gases (DNCG)

Dilute non-condensible gases are collected from non-pressurised tanks and equipment in the fibre line, evaporation plant, tall oil cooking plant and causticising plant. Gases from pressurised black liquor tanks should be led to the CNCG system. Leading of gases from non-pressurised black liquor tanks to the collection system for CNCG or DNCG should be considered on a case-by-case basis.

DNCG contain the same components as CNCG. DNCG include so much leakage air that their concentrations are below the explosion limit. Processes used to handle DNCG should ensure that these gases remain dilute in all operating circumstances.

The English abbreviation HVLC refers to High Volume Low Concentration gases. In the Recommended Good Practice published by the BLRBAC, the American term DNCG (Dilute Non-Condensible Gas) is used.

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#### 2.2 Dissolving tank and mixing tank vent gases

The ash and black liquor mixing tank can be connected to the DNCG or dissolving tank vent gases, for example via a dump tank. The collection system for mixing tank vent gases must be designed to keep the gases at a dilute concentration under any conditions.

Dissolving tank vent gases contain inorganic dust, ammonia and malodorous sulphur compounds. Vent gases have not traditionally been classified as noncondensible gases. However, vent gases introduced in to the recovery boiler furnace must be handled in accordance with the instructions for handling DNCG.

In the Recommended Good Practice published by the BLRBAC, the American term DTVG (Dissolving Tank Vent Gases) is used.

### 2.3 Concentrated non-condensible gas (CNCG)

Concentrated non-condensible gases originate mainly from the evaporation plant, stripping, methanol plant, firing liquor tank and heavy liquor tank. They may also come from the cooking plant.

Since CNCG contain inflammable gaseous compounds their handling involves a risk of explosion. This risk is eliminated by preventing air leaks into the system and by eliminating sources of ignition energy.

Reduced sulphur compounds (TRS, Total Reduced Sulphur) and especially turpentine are explosive in a wide concentration range.

The English abbreviations CNCG are used for Concentrated Non-Condensible Gas and LVHC for Low Volume High Concentration Gas.

SOG (Stripper Off-Gases) refers to concentrated non-condensible gases originating from the stripper. This gaseous mixture contains methanol (30% - 50% by weight) as well as TRS compounds, different terpenes and other high molecular weight organic compounds. The stripper off-gas is led directly to incineration or to a liquid methanol plant. If stripper off-gases are subjected to methanol liquefaction, the resulting NCG are led to the CNCG collection system. When SOG is led to

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methanol liquefaction, a more stable and reliable NCG incineration process will be achieved, also in disturbance situations in the evaporation plant and stripper.

Figure 2-1 shows two examples of a CNCG burner, showing for example CNCG inlet line, liquid methanol lance, flame scanners, flame arrester and support fuel lance.

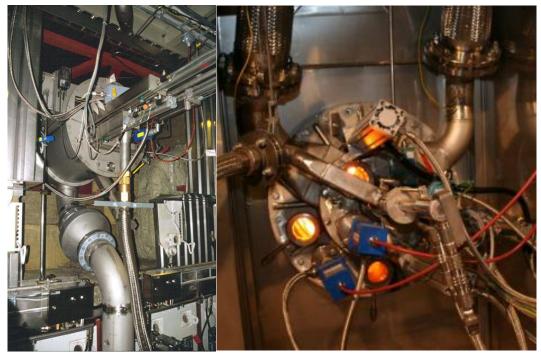


Figure 2-1. Examples of CNCG burners

# 2.4 Hydrogen sulphide

Hydrogen sulphide is a colourless, toxic, very easily flammable gas heavier than air, with the characteristic foul odour of rotten eggs. However, when reaching values of 100 ppm, an exposed person generally can no longer observe the odour of hydrogen sulphide. A leak of hydrogen sulphide in outdoor locations may cause ignition risks and in indoor locations explosion risks. Hydrogen sulphide corrodes several metals and plastics.

Hydrogen sulphide acts as a reducing agent and it may react violently with oxidising substances. The substance corrodes metals and generates metal sulphides. In water solutions hydrogen sulphide reacts as an acid. Hydrogen sulphide is generated when solutions containing sulphide, for example sodium sulphide,

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interact with acids, and it can be present in the whole mill area. It may spread over long distances along ducts and sewers. For this reason, gas alarms are installed in pulp mill areas where hydrogen sulphide may be present. When a detector notices a strong enough concentration of dangerous gas, the alarm lights installed in the system and close to measurement points are activated.

### 2.5 Methyl mercaptan

Methyl mercaptan is a colourless, very easily flammable, volatile and toxic gas, heavier than air. The detrimental effects of methyl mercaptan on health are similar to those of hydrogen sulphide.

## 2.6 Dimethyle sulphide / dimethyle disulphide

Under normal conditions, dimethyle sulphide and dimethyle disulphide are colourless liquids with a characteristic foul smell. Both compounds are easily flammable and explosive in contact with air.

## 2.7 Methanol

Pure methanol (CH<sub>3</sub>OH) is a colourless, almost odourless and toxic gas / liquid, but in a sulphate pulp mill methanol is contaminated by numerous malodorous compounds. Methanol is soluble in water in all volumetric ratios and can therefore easily be separated from a gas mixture in a scrubber.

Methanol vaporizes from black liquor during evaporation and ends up to foul condensate. Foul condensate is purified in a stripping column and methanol is condensed from stripper off gas (SOG) in a methanol column. Liquefied methanol is pumped via a storage tank to incineration.

# 2.8 Turpentine

Turpentine ( $C_{10}H_{16}$ ) is produced from volatile organic compounds (terpenes) in wood during chemical pulp production. Pure turpentine is a colourless and mildly odorous gas/liquid, but in sulphate pulp mills turpentine is contaminated by numerous malodorous compounds. A typical turpentine composition is shown in Table 2-2.

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Table 2-1. Typical turpentine composition				
Compound	Content, %			
Alpha-pinene	80 - 90			
Beta-pinene	5 - 10			
Delta-3-carene	5 - 10			
Other C <sub>10</sub> H <sub>16</sub> compounds	< 1			
Methyl mercaptan	0 - 5			
Dimethyl sulphide	0 - 12			
Dimethyl disulphide	0 - 1			

It is important to remove turpentine from NCG as effectively as possible, because it is explosive in a very wide concentration range. It shall be noted that turpentine has the lowest LEL, about 0.8 %, and even the flame propagation velocity of turpentine is low, the detonation velocity after explosion is high (100-130 m/s), while it is only about 1 m/s in turpentine free gas.

When collecting gases from terpene (turpentine vapour) containing sources, high concentrations can be avoided by condensation of turpentine compounds. These are separated in a scrubber by condensing with cold water. The scrubber is installed after the turpentine condenser in the NCG line. Separated turpentine is stored in turpentine tank.

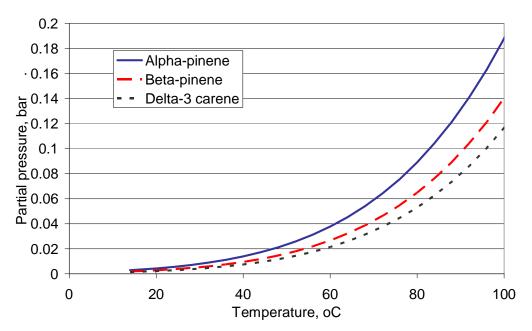


Figure 2-2. Partial pressures for some turpentine compounds, Drew et al., 1971.

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In spite of condensation, treated gas contains terpenes proportional to their partial pressure, Figure 2-2. This means that sources of DNCG possibly with a high content of terpenes must be diluted after collection or condensation. If the collection point maximum temperature is exceeded, the collected stream must be vented.

Sources of terpenes in NCG collection can be: softwood chip bins, foul condensate tanks, collection and weak liquor tanks, especially if they receive condensate containing turpentine, even if only occasionally. Also in shut-down and start-up situations, evaporated turpentine may vaporise with odorous gases on the surfaces of evaporation tanks or ducts.

In addition to NCG, turpentine can be separated from the bottom condensate in methanol distillation by means of a turpentine decanter. Turpentine separates to water surface, because it's lighter than water and poorly soluble. The raw turpentine is removed from decanter with overflow.

#### 2.9 Explosion limits

Lower Explosion Limit, LEL	Above this limit the concentration of inflammable gases may be high enough to cause an explosion (air as such does not explode).
Upper Explosion Limit, UEL	Below this limit the concentration of inflammable gases may be low enough to cause an explosion (fuel as such does not explode).
Explosive Region	Region between LEL and UEL (when above LEL there is enough fuel to cause explosion, when below UEL there is enough oxygen to cause explosion).

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### 2.9.1 Explosion limit formulas

The explosion limit is typically calculated based on the components in the gas mixture. The Ministry of Social Affairs and Health Decree on Chemical Classification Principles and Labelling (807/2001), Annex 1, Item 7.7.1, provides a formula for determining inflammability. It is based on <u>Standard ISO 10156</u> and its Tables 1 and 2, which provide calculation constants for different inflammable and inert gases. Table 2-1 resumes the characteristics of the different components of NCG in air.

 Table 2-2. Characteristics of different components of non-condensible gases in air. Burgess and Young 1992.

		Hydrogen sulphide	Methyl mercaptan	Dimethyl sulphide	Dimethyl disulphide	Turpentine (α pinene)	Methanol
Formula		$H_2S$	CH₃SH	(CH <sub>3</sub> ) <sub>2</sub> S	(CH <sub>3</sub> ) <sub>2</sub> S <sub>2</sub>	$C_{10}H_{16}$	CH₃OH
Molecular mass		34	48	64	94	132	32
Explosion limit LEL	% v/v	4.3	3.9	2.2	1.1	0.8	5.5
Explosion limit UEL	% v/v	45.0	21.8	19.7	16.1	6.0	36.5
Flame velocity	m/s			0.55		0.62	0.5
Auto-ignition temperature	°C	260	197 (340)	206	300	255	385 (465)
Flash point	°C	-82	-18	-49	24	34	11
Boiling point	°C	-60	6	38	110	150	65
Heat value HHV	MJ/kg	15	22	31	23	41	22
Volume weight of gas compared to air		1.19	0.87	2.14	3.24	4.7	1.11
Odour threshold	ppm	0.008	0.0004-0.003	0.001-0.01	0.003-0.011	100	100
Solubility in water		Yes	No	No	Poor	No	Yes

When defining ignition limits, that is to say explosion limits, it is advisable to use a method which is guaranteed to give safe limits. Explosion limits can be calculated according to different principles. For gas mixtures the calculation of explosion limits in Section 5.2. of <u>Standard ISO 10156/2010</u> can be used.

Another method is to examine the problem thermodynamically (Hokynar 1999). There is not much difference in the definition of the lower explosion limit, but the definitions of the higher explosion limit differ because of the dissimilar impact of inert gas in the two methods.

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#### 2.10 Abbreviations

Abbreviation	Finnish definition	English definition
BLRBAC	Amerikan soodakattilayhdistys	Black Liquor Recovery Boiler
		Advisory Committee
CH <sub>3</sub> SH (MM)	metyylimerkaptaani	methyl mercaptan
(CH <sub>3</sub> ) <sub>2</sub> S (DMS)	dimetyylisulfidi	dimethyl sulphide
$(CH_3)_2S_2$ (DMDS)	dimetyylidisulfidi	dimethyldi sulphide
CH <sub>3</sub> OH (MeOH)	metanoli	methanol
C <sub>10</sub> H <sub>16</sub>	tärpätti	turpentine
C <sub>2</sub> H <sub>5</sub> OH	etanoli	ethanol
CO <sub>2</sub>	hiilidioksidi	carbon dioxide
CO	hiilimonoksidi	carbon monoxide
H <sub>2</sub> S	rikkivety	hydrogen sulphide
H <sub>2</sub> O	vesi	water
NH <sub>3</sub>	ammoniakki	ammonia
NO	typpioksidi	nitric oxide
O <sub>2</sub>	happi	oxygen
SO <sub>2</sub>	rikkidioksidi	sulfur dioxide
CNCG	väkevät hajukaasut	concentrated non-condensible gas
DNCG	laimeat hajukaasut	dilute non-condensible gas
HAZOP	poikkeamatarkastelu	hazard and operability study
HEL	ylempi räjähdysraja	higher explosion limit
HVLC	laimeat hajukaasut	high volume low concentration
LEL	alempi räjähdysraja	lower explosion limit
LVHC	väkevät hajukaasut	low volume high concentration
NCG	hajukaasu	non-condensible gas
SHK	Ruotsin soodakattilayhdistys	Sodahuskommittén
SOG	stripperin kaasut	stripper off-gas
TRS	pelkistyneet rikkiyhdisteet	total reduced sulfur compounds
UEL	ylempi räjähdysraja	upper explosion limit
VOC	haihtuvat orgaaniset yhdisteet	volatile organic compounds
TLV	haitalliseksi tunnettu pitoisuus	threshold limit value

### **3** IMPACTS ON RECOVERY BOILER EMISSIONS

Incineration of NCG in the recovery boiler may affect recovery boiler emissions. Incineration of NCG may reduce the carbonate content and pH value of the recovery boiler precipitator ash. The additional sulphur in NCG is first seen as replacement of carbonate with sulphate in the electrostatic precipitator ash. When the carbonate content becomes low, the remaining sulphur will form SO<sub>2</sub>.

#### 3.1 Impacts on recovery boiler sulphur emissions

The extra sulphur contained in NCG always raises the sulphate content of recovery boiler ash and may therefore reduce its pH. Therefore, if there is not a sufficient carbonate buffer, the boiler's  $SO_2$  emissions may increase. Mill's with high sulphidity, low black liquor dry solids content, low heat value of liquor and low boiler load affect the boiler's  $SO_2$  emissions.

NCG should not be incinerated in a recovery boiler that already has sulphur emissions. When this is the case, the NCG should be incinerated for example in a separate incinerator with sulphur recovery. Such incinerators are for example NCG boilers and lime kilns with scrubbers.

#### 3.2 Impacts on recovery boiler TRS emissions

In modern boilers with efficient mixing of fuel and air and a NCG system that functions according to design specifications, the boiler's TRS emissions are not significantly increased, provided that the furnace temperature is at least 900 °C. When CNCG firing is started with low boiler load it is possible to get high  $SO_2$  and TRS emissions.

If DNCG is fed to the boiler above liquor guns, a small amount of NCG may pass without reacting along cold regions of the boiler wall.

The measurable impact in total flow has in practice been much below one ppm.

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#### 3.3 Impacts on recovery boiler fouling

See item 3.1, Impacts on recovery boiler sulphur emissions.

If the combustion conditions for NCG in the recovery boiler are not optimal and  $SO_2$  emissions are generated, there is a risk that boiler bank, economizers, and electrostatic precipitator may get fouled and also corrosion may occur especially if low ash pH prevails for long period.

#### 3.4 Impacts on recovery boiler NO<sub>X</sub> emissions

Especially CNCG contain nitrogen compounds. These nitrogen compounds consist mostly of ammonia, which is separated from black liquor in the evaporation plant.

In normal cooking, organic nitrogen compounds in the wood dissolve more or less completely in the alkaline cooking liquor and are thus transferred as part of the black liquor to the evaporation plant and further to the recovery boiler. Significant fraction of the organic nitrogen in the black liquor is transferred into the recovery boiler smelt as sodium cyanate, NaOCN. The cyanate nitrogen in the smelt passes into the green liquor through the dissolving tank along with the smelt's other salts. In the green liquor, alkaline hydrolysis gradually transforms cyanate nitrogen into ammonia.

The ammonia formed in the green liquor and in the white liquor partially evaporates into dilute malodorous gases. However, most of the ammonia continues as part of the white liquor back to the cooking. From the cooking, the ammonia passes into the black liquor together with the organic nitrogen compounds of the wood. The ammonia is finally quantitatively separated from the liquor in the evaporation plant, passing into concentrated malodorous gases and methanol.

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## 3.4.1 Impact of DNCG

DNCG typically account for 5...15% of the total amount of air fed into the recovery boiler. The nitrogen contained in DNCG is primarily ammonia. The ammonia content in dry gases can be assumed to be about 10 ppm. About 30% of the ammonia could be assumed to be converted into NO. If the boiler's NO level is about 100 ppm, the increase in the boiler's nitrogen oxide emissions would be:

$$NO_x = \frac{(100 + 0.3 * 0.1 * 10)}{100} - 1 \le 1\%$$

No measurable impact has been detected in practice, if DNCG are directed to the correct temperature range in the furnace.

#### **3.4.2** Impact of dissolving tank vent gases

The air contained in dissolving tank vent gases typically accounts for 5% of the total amount of air fed into the recovery boiler. The nitrogen contained in dissolving tank vent gases originates from the evaporation plant's secondary condensates or from the conversion into ammonia of nitrogen entering the dissolving tank with the smelt. The ammonia content in dry gases can be assumed to be about 100 ppm. About 30% of the ammonia could be assumed to be converted into NO. If the boiler's NO level is about 100 ppm, the increase in the boiler's nitrogen oxide emissions would be:

$$NO_x = \frac{(100 + 0.3 * 0.05 * 100)}{100} - 1 \approx 1\%$$

No measurable impact has been detected in practice, if dissolving tank vent gases are directed to the correct temperature range in the furnace. However, in some boilers slight NO<sub>X</sub> emission increase has been reported when dissolving tank vent gases are led into the tertiary air level.

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## 3.4.3 Impact of CNCG

CNCG typically account for 0.2...3% of the total amount of air fed into the recovery boiler. The nitrogen contained in CNCG is primarily ammonia. The ammonia content in dry gases can be assumed to be about 2000 ppm. About 30% of the ammonia could be assumed to be converted into NO. If the boiler's NO level is about 100 ppm, the increase in the boiler's nitrogen oxide emissions could be:

$$NO_x = \frac{(100 + 0.3 * 0.01 * 2000)}{100} - 1 \approx 6\%$$

#### 3.4.4 Impact of methanol

Approximately 10 kg/ADt of methanol is generated, depending on the wood raw material used. The ammonia content in liquid methanol may be around 2%. The ammonia content in methanol may be assumed to be approximately 0.2 kg/Adt. It can therefore be assumed that around 30% of the ammonia is converted into NO. If the boiler's NO content is 200 mg/Nm<sup>3</sup>, 3.5 Nm<sup>3</sup>/kg of combustion gas is generated and the amount of liquor dry solids is 1600 kgDS/ADt. Then the increase in the boiler's nitrogen oxide emissions may be as follows:

$$NO_x = \frac{(200*3,5*1600/1000000+0,3*0,2)}{200*3,5*1600/1000000} - 1 \approx 5\%$$

#### 3.5 Impacts on other recovery boiler functions

In modern boilers with efficient mixing of fuel, air and sufficient base load operating according to design specifications, no impacts on other recovery boiler operation parameters have been observed. For example, changes in reduction rate have not been reported.

Incineration of NCG gases generally reduces the mill's total sulphur emissions. This, however, affects the mill's chemical balances and tends to increase sulphidity. Therefore the sulphur balance at a mill has to be examined on a case-bycase basis.

Water vapour is introduced into the boiler with dissolving tank vent gases and DNCG, which may lower the boiler's capacity somewhat, depending on water vapour content. Figure 3-1 presents the maximum amount of water vapour contained in air at a specific temperature. Warm air can hold more vapour than cold air. The incineration of CNCG, methanol and turpentine increases boiler steam generation slightly. In that case the design of the water and steam systems has to be checked before starting incineration, especially in existing recovery boilers.

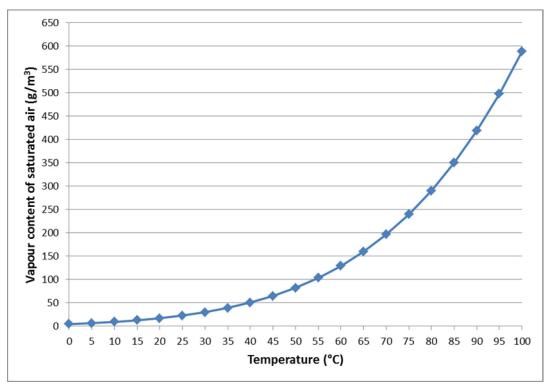


Figure 3-1. Saturated water vapour content in air as a function of temperature.

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## 4 RISKS AND CORROSION RELATED TO NCG SYSTEMS

Typical risks related to NCG incineration systems include explosion risk (gas concentration and ignition by sparks, for example as a result of overpressure in the furnace), danger of toxication, condensate draining problems (water entering the furnace) and corrosion/erosion.

The Finnish Recovery Boiler Committee's recommendation is that a hazard and operability study (e.g. HAZOP) shall always be made when NCG system is modified together with the supplier of the NCG system.

In addition, NCG incineration may cause process-related problems, such as sulphur emissions from the boiler, plugging of economiser and other boiler heating surfaces and combustion disturbances in the furnace.

#### 4.1 Leakage of non-condensible gases into manned areas

NCG may leak from joints, valves, drains or failure areas. The concentrations of reduced sulphur compounds and methanol in NCG are so high that there is a danger to get toxicated. If a leak occurs into the boiler house or some other manned area, the entire house or space has to be evacuated, duly ventilated and concentrations measured to confirm that it is again safe to work in.

NCG can be released into manned enclosures typically from condensates during maintenance work. Possible leakage sources are water seals in the NCG system, as well as the safety devices in the system. Special care is required when operating methanol and turpentine burners. Even a very small leak may cause a major odour problem.

Because CNCG lines are kept at overpressure after the ejector in the recovery boiler building, there may develop a danger of toxication in the recovery boiler building when there is a leak in the NCG line. In ineffectively ventilated areas there may also be an explosion risk.

In accordance with the instruction entitled "Maximum concentrations of impurities in the working place" issued by the Finnish Ministry of Social Affairs and Health,

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the maximum allowed indoor hydrogen sulphide concentration is 5 ppm (7 mg/m<sup>3</sup>) / 8 h and 10 ppm (14 mg/m<sup>3</sup>) / 15 min. These so-called TLV values (threshold limit value) are the lowest concentrations of airborne chemicals in the workplace that could cause harm to workers.

Mills have typically both fixed and portable hydrogen sulphide and VOC meters. The fixed meters activate blinking warning lights and buzzers if the hydrogen sulphide or VOC content in the air is too high. When placing the meters, for instance air flows and working area should be taken into consideration. Regular functional tests should be made of both fixed and portable meters and there should be instructions for the meters in the quality systems. The tests carried out should be documented.

Maintenance or repair work on NCG equipment requires special permits.

#### 4.1.1 Odour

Sulphur compounds numb the sense of smell so it is not advisable to trust the nose alone. This may result in a lethal situation, unless appropriate protective action is taken. Employees working with equipment containing NCG must familiarise themselves with the operating safety instructions concerning DNCG and CNCG.

### 4.1.2 Safety equipment

A pressurized air mask is the only safety equipment that protects from the effects of NCG. Gas masks and personal breathing equipment are meant only for leaving a danger zone.

### 4.2 Condensate draining problems

If water vapour is allowed to condense in a NCG pipeline, there is a risk of a smelt water explosion, if this water enters the recovery boiler.

Special attention must be paid to water drains to confirm that condensate can be removed from all lines in a comprehensive manner.

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### 4.2.1 Overflowing of condensate trap

A common problem with NCG systems is the occasionally large volume of condensate. Condensate traps close to the recovery boiler shall be provided with high-level alarm and, if necessary, with interlocking to lead NCG away from incineration.

#### 4.2.2 Drying out of water seals

Drying of water seals is accelerated when NCG are heated above condensation temperature. To prevent water seals from drying out, they should always be provided with a sufficient fresh water supply and equipped with flow alarms.

Measures should also be taken to prevent water seals from drying during shutdowns.

#### 4.2.3 Plugging of water seals

NCG carry with them small amounts of liquor foam/soap, which may accumulate at the lowest points of the line, for example at condensate drain points. If the drain pipe diameter is not large enough, complete plugging of the pipe may occur.

#### 4.3 Explosion risks in NCG lines

Transfer and incineration of CNCG shall be designed so that there is no explosion risk under any circumstances. An explosion risk arises if air leaks into CNCG. The concentration of CNCG is maintained above the upper explosion limit by ensuring system sealing.

Transfer and incineration systems for DNCG are designed to keep the concentration of gases below the lower explosion limit. The concentration of DNCG is kept below the explosion limit by ensuring sufficient dilution by air. In some cases an explosion risk may arise when water vapour in DNCG is eliminated by condensation and gas concentration approaches the lower explosion limit.

Ignition requires ignition energy such as static electricity, heat or an electrical spark. Spark generation is best avoided by making sure that groundings, structures and equipment are selected and installed properly.

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#### 4.3.1 Shut-down and start-up situations

Special attention needs to be paid to the concentrations of DNCG during shut-down and start-up situations. Explosions in recovery boilers caused by NCG have several times been related to DNCG systems, where the gas concentration has risen too much during shut-downs and disturbance situations. A typical problem is the accumulation of explosive gases in the pipeline during a shut-down and their volatilization when NCG collection is started.

#### 4.4 Gas explosion in boiler

NCG are a mixture of inflammable components, oxygen and inert gas (nitrogen, water vapour). As is always the case when handling inflammable gases, there is a risk of explosion in the furnace. A gas explosion occurs if fuel is fed into the furnace without ensuring immediate combustion, after which the mixture absorbs so much energy that it is ignited.

#### 4.5 Smelt-water explosion in boiler

Water condensate getting into the furnace from the NCG line may cause a smeltwater explosion. To prevent this from happening, DNCG and dissolving tank vent gases must be sufficiently heated so that the major part of the water droplets turns into vapour and the gas lines are sloped and equipped with a sufficient amount of condensate drains. When designing drain systems, attention should be paid for example to the size, amount and location of the drains.

A smelt-water explosion means extremely rapid vaporisation of water that gets into contact with the cooking chemical. The pressure wave caused by this vaporisation may damage the furnace and thus cause a leak of NCG/water/steam into the boiler house.

### 4.6 Corrosion problems

The burning of NCG in recovery boilers has not been found to increase corrosion.

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## 4.7 Sparking / static electricity

For an explosion to occur there must be some kind of initial energy, such as a spark. To confirm good safety, NCG lines are potentially balanced from the collection point forward. The objective of potential balancing is to prevent the appearance of dangerous voltage differences between conducting parts that may be touched simultaneously. For instance in flanges, hatches and connections where a galvanic isolation may be formed for example due to isolation materials, potential balancing must be performed. Potential balancing shall be made according to the given instructions and verified with a field log.

## 5 DNCG SYSTEMS IN A RECOVERY BOILER

Dilute non-condensible gases are not fuel. They primarily consist of air and water vapour. According to the Finnish Chemicals Act, DNCG are generally classified as harmful, so equipment purchases, engineering, installation and operation must be handled accordingly.

To confirm the operating safety of the recovery boiler, necessary precautions must be taken to prevent water from entering the boiler when DNCG are incinerated. DNCG are cooled down (part of the water contained in the gases is condensed), transported by a fan and heated up to confirm evaporation of any water droplets before incineration. NCG lines are equipped with condensate drains to prevent water from accumulating in the gas line and from there entering the boiler.

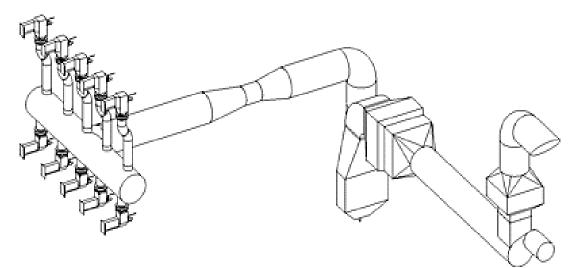


Figure 5-1. Example of a duct system for dilute non-condensible gases

### 5.1 Composition and amount

Dilute non-condensible gases consist of, among other things, tank and equipment vent gases from the pulp mill's fibre line, vent gases from the evaporation plant's tank farm, the causticising plant's vent gases, etc. DNCG amount to  $300 - 400 \text{ m}^3\text{n}/\text{ADt}$ , and their sulphur content is 0.1 - 0.5 kgS/ADt. DNCG are typically treated in a scrubber-type vent gas cooler, which removes moisture and so reduces the amount of gases to be handled. Typical amounts of DNCG collected from various pulp mill departments are shown in Table 5-1.

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Department	kg S/ADt	m <sup>3</sup> n/ADt
Vent gases from continuous cooking	0.1 – 0.5	100 - 400
Vent gases from Superbatch cooking (evacuation air, vents from non-pressurised tanks)	0.1 – 0.5	150 – 300
Washing plant vent gases	0.05 – 0.1	100 – 200
Tall oil cooking plant vent gases	0.05 - 0.2	2-3
Tank vent gases, evaporation plant (atmospheric pressure tanks)	0.1 – 0.4	20 – 30
Causticising plant-lime kiln area	0.01 – 0.1	5 – 10
TOTAL	0.1 – 0.5	300 - 400

#### Table 5-1. Amount of DNCG collected from different departments at a temperature of 40 $^\circ\mathrm{C}$

The concentration of DNCG should continuously be kept below the explosion limit and any increase in concentration should be prevented. When the concentration and moisture content are kept low, DNCG can be handled at the boiler plant in the same way as other combustion air.

When incineration of DNCG is taken into use for the first time at the mill or the process is modified, concentrations in the gas lines at different collection points must be measured to verify the contents of DNCG in different collecting points. Examples of DNCG analyses are given in Table 5-2. The contents of the DNCG components vary extensively depending on the mill and measuring points.

	Mill A	Mill B	Mill C	Mill D	Mill E	Mill F
Component	ppm	ppm	ppm	ppm	ppm	ppm
H <sub>2</sub> S	*	*	1	0	725	1
MM, CH₃SH	200	40	70	2	14	2
DMS, (CH <sub>3</sub> ) <sub>2</sub> S	1 000	60	160	643	1 530	784
DMDS, $(CH_3)_2S_2$	90	*	270	1	10	365
Turpentine, $C_{10}H_{16}$	1 500	15	*	69	470	12 400
MeOH, CH₃OH	900	150	*	834	6 943	2 046
Ethanol, C <sub>2</sub> H <sub>5</sub> OH	80	*	*	*	*	*
Oxygen, O <sub>2</sub>	*	*	*	*	*	*
Ammonia, NH <sub>3</sub>	200	*	*	*	*	*
Water, H <sub>2</sub> O	70 000	50 000	*	*	*	*
Carbon dioxide, CO <sub>2</sub>	*	300	*	*	*	*

Table 5-2. Examples of	DNCG analyses at	the point of origin.
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\*) Not analysed or below detection limit

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Special attention needs to be paid for preventing the gas concentration in chip silo vent gases from rising too high in disturbance situations. In the event of a disturbance in the chip silo, vent gases from the silo must not be conducted to the collection system for DNCG. Table 5-3 shows the recommended maximum concentrations for DNCG before incineration. DNCG are typically much below 10% of LEL.

Table 5-3. Maximum recommended concentrations of DNCG before incineration

Compound	Limit	Note
Air content, vol-%	> 90	
Water content, vol-%	< 7	40 °C (after condensing)
Water content, vol-%	< 12	50 °C (after condensing)
Sulphur content TRS, ppm	<200	
Turpentine content, ppm	< 1000	
Methanol content, ppm	< 1000	

In addition, it needs to be determined to where turpentine-containing condensates can be diverted safely in the event of a disturbance in the cooking plant. There are examples of cases where a careless connection has caused a significant increase in the turpentine content of the condensate during a cooking plant disturbance.

DNCG are typically fed into the recovery boiler as a part of the boiler's combustion air. Because of the smelt-water explosion risk caused by the condensate entering the furnace, it is not recommended to feed DNCG into primary air.

### 5.2 Cooling / heating

Condensate from DNCG must not be allowed to enter the recovery boiler furnace. The amount of water vapour entering the furnace with DNCG must be minimised. The temperature of DNCG should preferably be 40-50 °C after the condenser.

DNCG are recommended to be heated to 30 °C above the condensate temperature to minimise the entrance of water drops into the furnace.

# 5.3 Starting / tripping logic for incineration of DNCG

The purpose of this section is to describe the process conditions to be fulfilled by the interlocks controlling the incineration of DNCG. The focus is on the most essential conditions that a safe automation system (SIS) must fulfil. Because of

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differences in equipment design, process connections and technical implementation, the interlocks of any recovery boiler will also include other conditions than those presented here.

This recommendation does not cover interlocking related to the start and operation of the collection of DNCG, though these are often partly implemented in the same system as interlocking related to incineration. These interlocking have to be defined case by case.

The Finnish Recovery Boiler Committee recommends that the DNCG system has been in use for a sufficiently long time (for example over one hour). Several compounds can be condensed in the ducts. It is necessary to vaporise and vent out the inflammable gas components from the system. If possible, the collection of DNCG should be operated during shut-downs. The objective is to prevent the concentration of DNCG to explosive area in the system.

It must be possible to supervise the incineration of DNCG in the recovery boiler as well as to control starting and stopping DNCG incineration from the same main control room where the other activities related to the operation of the recovery boiler are controlled.



## 5.3.1 Starting logic for introducing DNCG

DNCG can be introduced into the boiler furnace when e.g. the conditions below are fulfilled, Table 5-4. Because of differences in commissioning year, equipment design, process conditions and technical implementation, the interlocks of any DNCG incineration will also include other conditions than those presented here.

Table 5-4. To admit DNCG to the recovery boiler, the following conditions should be fulfilledConditionPurpose of condition

- 1 Boiler steam load / feed water flow over 15% of boiler nominal load. **This limit shall be defined on a case-by-case basis**
- 2 DNCG gas fan is on
- 3 Sufficient pressure in the duct system ahead of shut-off valve
- 4 Sufficient flow in the duct system ahead of shut-off valve
- 5 Temperature after cooling below temperature limit
- 6 Temperature before introduction into boiler/after heater above temperature limit
- 7 Ventilation outlet to the roof (bypass) has been in operation long enough
- 8 Condensate pocket level in NCG system (if exists) below upper limit

Confirm sufficiently stable furnace conditions to oxidise TRS compounds (temperature, retention time) Verify that there is sufficient flow in the duct to prevent flame propagation backward in the pipeline (burn-back)

Verify that there is sufficient flow in the duct to prevent flame propagation backward in the pipeline (burn-back)

Verify that there is sufficient flow in the duct to prevent flame backward progression in the pipeline (backfire)

Reduce the amount of water vapour and gas volume

Prevent water droplets from entering the boiler

Prevent concentration of DNCG in the duct system

Prevent condensate entering the furnace.



Figure 5-2. Installation phase of a mill's DNCG incineration system.

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## 5.3.2 Tripping logic for introducing DNCG

The introduction of DNCG to the boiler furnace has to be stopped if any of the conditions below is fulfilled, Table 5-5. Because of differences in commissioning year, equipment design, process conditions and technical implementation, the interlocking logic of any DNCG incineration will also include other conditions than those presented here.

Table 5-5. Any of the following conditions will disallow introduction of DNCG to the recovery boiler:

	Condition	Purpose of condition
1	Boiler steam load / feed water flow is below 15% of boiler nominal load. <b>This limit shall</b> <b>be defined on a case-by-case basis</b>	Confirm sufficiently stable furnace conditions to oxidise TRS compounds (temperature, retention time)
2	Emergency shut-down activated	Prevent introducing of DNCG when the boiler is not in accepted condition
3	DNCG fan stopped	Prevent flame propagation backward in the pipeline (burn-back)
4	Temperature after cooling above temperature limit	Gas moisture content too high
5	Temperature before introduction into boiler/after heating below temperature limit	Amount of water droplets too high
6	Pressure in non-condensate gas duct below the lower limit	Prevent flame propagation backward in the pipeline (burn-back)
7	Condensate pocket level in DNCG system above upper limit	Prevent condensate from entering the furnace.

#### 5.4 Ducts

DNCG must be prevented from leaking into the boiler house and the length of the duct inside the boiler house must be minimised.

#### 5.4.1 Flow

It is recommended to measure the flow of DNCG going to incineration. The flow measurement device is recommended to locate as close as possible to the boiler's gas inlet.

### 5.4.2 Potential balancing

No potential balancing is required for DNCG.



## 5.5 Valves / dampers

The valves / dampers for the DNCG incineration system shall be selected with care. Special attention shall be paid to their sealing characteristics. Normally, effectively sealing throttle valves / dampers are used for large duct sizes.

The DNCG line should have automatic shut-off valves with "fail-close" actuator which will close DNCG introduction to the recovery boiler automatically if operating energy is turned off. At the same time valve of the alternative location or bypass duct must open (fail-open). Valves must be provided with limit switches indicating position to the automation system.

#### 5.6 Fan

The sealing characteristics of the fan must be sufficient and the fan must be equipped with a condensate draining system.

#### 5.7 Make-up air inlet

DNCG systems may incorporate a make-up air inlet (excess air inlet) to allow air to be mixed into the dilute gases. If the safety of NCG is dependent on the operation of the make-up air inlet, special care must be taken to confirm that the make-up air supply cannot be switched off for any reason.

For the above mentioned reasons, air addition must be sufficiently supervised and measured, for example by flow measurements, and necessary interlocking must be installed for insufficient air flow.

Dilution air inlet must be designed so that NCG backflow to working areas

#### 5.8 Scrubbers / condensers

The DNCG system shall incorporate a sufficient number of scrubbers or condensers to remove the water vapour and VOC (for example turpentine) contained in the gases and reduce the collected gas volume.

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### 5.9 Droplet separator

A droplet separator should preferably be used at the incineration end of the DNCG duct before the gases are heated up, and always after DNCG have been cooled or treated in a scrubber.

#### 5.10 Condensate draining

DNCG lines have to be equipped with condensate drains. Condensates shall primarily be conducted as a separate system to the foul condensate treatment system.

In designing condensate draining, special attention shall be paid for example to drain size, number and location. The last condensate drain is recommended to locate as close to the recovery boiler as possible so that the length of the duct from this drain to the furnace is minimised. This drain should have condensate pocket with limit switch.

#### 5.10.1 Size of condensate drain lines

Because of the risk of plugging, the recommended minimum diameter for condensate drains is 50 mm. The condensate drain lines closest to boiler should be at least 100 mm. If there is a possibility of additional water (e.g. washing water) feed into the system, then condensate drain lines shall be sized accordingly.

### 5.10.2 Duct slopes and locations of condensate drains

Ducts and pipes must slope towards the condensate drains. Condensate draining against flow is very difficult. The recommended slope for ducts, elsewhere than in the recovery boiler plant, in the direction of the gas flow is 1:100 and counter to the direction of the gas flow 1:25.

Because of the risk of water getting into the furnace, the preferred slope for ducts in recovery boiler plants in the direction of the gas flow is 1:100 and counter to the direction of the gas flow 1:1 or more. A condensate drain must be installed before every point where the NCG line angles upward. If the recommended slopes cannot be achieved in some duct sections, the condensate drains in this part of the system must be designed with special care.

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# 5.10.3 Water seals

Condensate outlet lines shall be equipped with water seals or with a common seal tank (condensate collection tank). In this way, DNCG are prevented from leaking via the condensate drains.

To prevent water seals from drying out, they shall be equipped with level indicators or provided with a continuous water flow controlled by flow indicators.

To confirm that the pressure in the DNCG duct will not rise so high as to drain the water seal, the difference between the water levels in the water seal must be allowed to vary by at least 10 kPa, or by an amount corresponding to the duct's design pressure. 10 kPa corresponds to a water level variation of 1 m in the water seal.

# 5.11 Flame arrester

There is no need to use a flame arrester in DNCG system.

# 5.12 Bypass

The bypass duct for DNCG must be led to as high a point as possible. Normally, the bypass duct is led to the roof of the recovery boiler plant or to the stack.

# 5.13 Underpressure protection device

DNCG lines can be equipped with underpressure protection, if the pipeline's design and fan suction so demand.

# 5.14 Overpressure protection device

There is no need to use overpressure protection in DNCG lines.

# 5.14.1 Rupture disc

There is no need to use a rupture disc in DNCG lines. If rupture discs are used in the systems as pressure protection, their condition shall be controlled by an alarm in the automation system. The outlet of the rupture disc shall be aligned in a safe direction.

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# 5.15 Concentration measurement

There is no need for continuous concentration measurement in DNCG lines.

The Finnish Recovery Boiler Committee recommends measuring the concentrations of DNCG at sources when any equipment changes are made at that point.

In addition, the Finnish Recovery Boiler Committee recommends measuring the average concentration of sulphur and oxygen in DNCG to incineration at least once a year.

# 6 DISSOLVING TANK VENT GAS SYSTEMS AT THE RECOVERY BOILER

Dissolving tank vent gases are DNCG primarily consisting of air and water vapour. To recover odorous sulphur compounds contained in dissolving tank vent gases and to reduce dust emissions, these gases are being incinerated in the recovery boiler. The Finnish Recovery Boiler Committee recommends incineration of dissolving tank vent gases in the recovery boiler.

For instance, vent gases from the mixing tank, vent gases from the ash handling process and the mill's DNCG can be led to the dissolving tank vent gas system.

To confirm safe operation of the recovery boiler, water must be prevented from entering the boiler when dissolving tank vent gases are incinerated.

Dissolving tank vent gases are scrubbed, cooled, blown with a fan and heated up in order to vaporize water droplets before incineration. Vent gas lines are equipped with condensate drains to prevent water from accumulating in the vent gas line and thus from entering the boiler.

#### 6.1 Composition and amount

Dissolving tank vent gases primarily originate from leakage air, steam due to boiling of the green liquor in dissolving tank caused by the heat in the smelt and smelt-atomising steam. The most problematic aspect with a view to the treatment are the small green liquor droplets in dissolving tank vent gases which, when drying, tend to foul/plug the vent gas system.

Typical dissolving tank vent gas volumes and compositions are shown in Table 6-1

Table 0-1. Dissorving tank vent gas volumes and co	mpositions, Rantane	11/07
Vent gas volume from dissolving tank	m³n/kgds	0.4 - 0.8
Vent gas temperature from dissolving tank	°C	85 - 95
Vent gas moisture content from dissolving tank	vol-%	40 - 80
Vent gas total particulates from dissolving tank	mg/m³n (dry)	1000 - 5000
Vent gas TRS from dissolving tank	mg/m³n (dry)	150 - 700
Vent gas total sulphur after scrubber	kg S/ADt	0.01 - 0.1
Vent gas total particulates after scrubber	mg/m³n	100 - 200
Vent gas TRS after scrubber	mg/m³n	1 - 10

 Table 6-1. Dissolving tank vent gas volumes and compositions, Rantanen 1987

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Dissolving tank vent gases can be fed into the recovery boiler for example mixed with air or with other DNCG. Another possibility is to introduce the dissolving tank vent gases to boiler through separate nozzles.

# 6.2 Mixing tank vent gases

If mixing tank vent gases are led to the dissolving tank vent gas system, attention must be paid to their fouling effect. A proper scrubber can be added to the mixing tank vent gas system.

If mixing tank vent gases are led to the furnace as a system of its own, the vent gas incineration recommendations and interlocking must be taken into account.

# 6.3 Cooling / heating

Dissolving tank vent gas condensate must not be allowed to enter the furnace. The amount of water vapour entering the furnace together with dissolving tank vent gases must be minimised. The dissolving tank vent gas system shall be equipped with a gas cooler. Gas cooler is used to remove water vapour, thus reducing the amount of moisture going to the furnace. It must be possible to wash the cooler while the recovery boiler is in operation.

The temperature of dissolving tank vent gases after the cooler should preferably be 40-50  $^{\circ}$ C.

Dissolving tank vent gases should preferably be heated to a temperature of  $30 \,^{\circ}C$  above condensing temperature, to prevent water droplets from getting into the furnace.

# 6.4 Starting / tripping logic for the incineration of vent gases

The purpose of this section is to describe the process conditions to be fulfilled by the interlocking logic controlling the incineration of dissolving tank vent gases. The focus is on the most vital conditions that a safe automation system (SIS) must fulfil. Because of differences in equipment design, process connections and technical implementation, the interlocking logic of any recovery boiler will also include other conditions than those presented here.

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It must be possible to supervise the incineration of dissolving tank vent gases in the recovery boiler, as well as to control starting and stopping dissolving tank vent gas incineration from the same main control room where other activities related to the operation of the recovery boiler are controlled.

#### 6.4.1 Starting logic for introducing dissolving tank vent gases

Dissolving tank vent gases can be introduced into the recovery boiler furnace when the conditions below are fulfilled, Table 6-2. Because of differences in commissioning year, equipment design, process conditions and technical implementation, the interlocking logic of any vent gas incineration will also include other conditions than those presented here.

Table 6-2. To admit dissolving tank vent gases to the Recovery Boiler, the following conditions should be fulfilled: ....

-

	Condition	Purpose of condition
1	Boiler steam load/feed water flow is over 15% of boiler nominal load. <b>This limit shall</b> <b>be defined on a case-by-case basis</b>	Confirm sufficiently stable furnace conditions to oxidise TRS compounds (temperature, retention time)
2	Dissolving tank vent gas fan is on	Verify that there is sufficient flow in the duct to prevent flame propagation backward in the pipeline (burn-back)
3	Sufficient pressure in duct system ahead of shut-off valve	Verify that there is sufficient flow in the duct to prevent flame propagation backward in the pipeline (burn-back)
4	Duct flow before shut-off valve sufficient (if separate nozzles)	Verify that there is sufficient flow in the duct to prevent flame backward progression in the pipeline (backfire)
5	Temperature after cooling (ahead of heater) below temperature limit	Reduce amount of water vapour and gas volume
6	Temperature before introduction to boiler/after heater above temperature limit	Prevent water droplets from entering the boiler
7	Condensate pocket level in NCG system (if exists) below upper limit	Prevent condensate entering the furnace

#### 6.4.2 Tripping logic for introducing dissolving tank vent gases

The introduction of dissolving tank vent gases into the recovery boiler furnace has to be stopped if any of the conditions below is fulfilled, Table 6-3. Because of differences in commissioning year, equipment design, process conditions and technical implementation, the interlocking logic of any vent gas incineration will also include other conditions than those presented here.

Destary Detter

Table 6-3. Any of the following conditions will divert dissolving tank vent gases from the

	Recovery Boiler:	
	Condition	Purpose of condition
1	Boiler steam load/feed water flow is below 15% of boiler nominal load. <b>This limit shall</b> <b>be defined on a case-by-case basis</b>	Confirm sufficiently stable furnace conditions to oxidise TRS compounds (temperature, retention time)
2	Emergency shut-down activated	Prevent introduction of NCG when the boiler is not in accepted condition
3	Dissolving tank vent gas fan stopped	Prevent flame propagation backward in the pipeline (burn-back)
4	Temperature after cooling (ahead of heater) rises above temperature limit	Reduce amount of water droplets and gas volume
5	Temperature before introducing into boiler/after heater below temperature limit	Prevent water drops entering the boiler
6	Condensate pocket level above upper limit	Prevent condensate entering the furnace

#### 6.5 **Ducts**

Dissolving tank vent gases must be prevented from escaping into the boiler house and the length of the duct inside the boiler house shall be minimised.

Because of the risk of corrosion, the ducts and nozzles for dissolving tank vent gas incineration shall be made from stainless steel EN1.4301 (SS2333) or better.

#### 6.5.1 Flow

The flow of dissolving tank vent gases can be measured. The flow measuring point shall be close to the point where dissolving tank vent gases are introduced into the boiler.

#### 6.5.2 **Potential balancing**

No potential balancing is required for dissolving tank vent gas ducts.

#### 6.6 Valves / dampers

The valves/dampers for dissolving tank vent gas incineration shall be selected with care. Special attention shall be paid to the valve sealing characteristics. Normally, effectively sealing valves/dampers are used.

The dissolving tank vent gas line should have automatic shut-off valve with "failclose" actuator which will close vent gas introduction to the recovery boiler automatically if operating energy is turned off. At the same time valve of the

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bypass duct must open (fail-open). Valves must be provided with limit switches indicating position to the automation system.

# 6.7 Fan

The fan structure must be sufficiently tight and the fan must be equipped with a condensate draining system.

# 6.8 Scrubber

The dissolving tank vent gas system shall incorporate an effective cooling scrubber to remove dust and water vapour. It must be considered to wash the scrubber and the main equipment while the recovery boiler is in operation.

# 6.9 Droplet separator

A droplet separator after gas cooling is recommended in the dissolving tank vent gas system. Droplet separator removes possible water droplets from gas before incineration.

# 6.10 Washing of droplet separator and vent gas heater

Dissolving tank vent gases include a lot of fine dust which plug droplet separators, heater and ducting. When water washing of the equipment is carried out then extra care must be paid on proper condensate / water removal. If condensate pockets limit switches are indicating level the washing must be stopped. During extensive washing, vent gases shall be by-passed.

# 6.11 Condensate draining

Dissolving tank vent gas lines must be provided with condensate drains. Condensates shall primarily be conducted to the dissolving tank or to the treatment system for foul condensate.

In designing condensate drains, special attention shall be paid for example to the size, number and location of the drains. The last condensate drain is recommended to locate as close to the recovery boiler as possible so that the length of the duct from this drain to the furnace is minimised. Drain lines closest to the boiler should have condensate pockets with limit switches.

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# 6.11.1 Size of condensate drains

Because of the risk of plugging, the recommended minimum diameter for condensate drains and condensate lines starting from these is 50 mm. The condensate drain line closest to boiler should be at least 100 mm. If there is a possibility of additional water (e.g. washing water) feed into the system, then condensate drain lines shall be sized accordingly.

# 6.11.2 Duct slopes and locations of condensate drains

Ducts and pipes must slope towards the condensate drains. Condensate draining against flow is very difficult. The recommended slope for ducts, elsewhere than in the recovery boiler plant, in the direction of the gas flow is 1:100 and counter to the direction of the gas flow 1:25.

Because of the risk of water getting into the furnace, the preferred slope for ducts in recovery boiler plants in the direction of the gas flow is 1:100 and counter to the direction of the gas flow 1:1 or more. A condensate drain must be installed before every point where the vent gas line angles upward. If the recommended slopes cannot be achieved in some duct sections, the condensate outlets in this part of the system must be designed with special care.

# 6.11.3 Water seals

Condensate drain lines must be provided with water seals or a common seal tank (condensate collection tank). In this way, NCG are prevented from leaking via the condensate drains. To prevent water seals from drying out, they shall be equipped with level indicators or with a continuous water flow controlled by flow indicators.

To confirm that the pressure in the dissolving tank vent gas duct will not be sufficient to drain the water seal, the difference between the water levels in the water must be allowed to vary by at least 10 kPa, or by an amount corresponding to the duct's design pressure. 10 kPa corresponds to a water level variation of 1 m in the water seal.

#### 6.12 Flame arrester

There is no need for a flame arrester in dissolving tank vent gas ducts.



# 6.13 Bypass

The bypass for dissolving tank vent gases must be led to as high a point as possible. Normally, the bypass duct is led to the roof of the recovery boiler plant or to the stack.

# 6.14 Overpressure protection

The dissolving tank vent gas system must be able to withstand the overpressure generated by the fan. In addition, there must be a separate duct from the dissolving tank to the roof of the recovery boiler plant which is opened by overpressure in the dissolving tank.

# 6.14.1 Rupture disc

There is no need for a rupture discs in dissolving tank vent gas ducts.

# 6.15 Concentration measurement

There is no need for continuous concentration measurement of dissolving tank vent gases.

# 7 INCINERATION OF CNCG IN THE RECOVERY BOILER

Concentrated non-condensible gases are a low-calorific fuel and the system for incinerating such gases must comply with the same recommendations and regulations concerning safety and logics as for any other explosive gases.

Sources for CNCG are for example non-condensible gases from the vacuum pit of the evaporation plant, gases from the stripper and methanol distilling plant, vent gases from the foul condensate tank, gases from cooking plant condensers, gases from turpentine system and gases from pressurised firing liquor tank. Every effort must be made to prevent leakage of air into CNCG under any circumstances.



Figure 7-1. Lower part of the recovery boiler furnace with a separate CNCG burner opening in the centre.

# 7.1 Composition and amount

The total amount of sulphur in CNCG in a modern chemical pulp mill is in the range of 2–4 kgS/ADt. This amount is increased considerably if black liquor is evaporated to a high dry solids content (over 80%). For process reasons, the amount of CNCG may vary widely at different sources in time. Typical

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departmental amounts of CNCG collected from different sources in a chemical pulp mill are shown in Table 7-1.

Department	kg S/ADt	m <sup>3</sup> n/ADt
Batch cook blowing	0.4 – 0.8	5 - 15
Batch cook gassing	0.1 – 0.2	1.0 – 3.0
Continuous cooking	0.1 – 0.4	1.0 – 4.5
Stripper	0.5 – 1.0	15 –25
Evaporation plant	0.4 – 0.8	1 – 10
Methanol processing	0.5 – 1.0	1.0 – 2.0
Black liquor heat treatment	2 – 3	1.5 – 3.0
Concentrator	2 – 5	1.5 – 6.0

CNCG contain significant amounts of sulphur compounds and ammonia. Examples of analyses of CNCG are shown in Table 7-2. Depending on their components, CNCG are classified as extremely toxic, toxic or inflammable. Heat values of CNCG components are presented in Table 7-3.

-	Mill A	Mill B	Mill C	Mill D
Component	ppm	ppm	ppm	% vol
$H_2S$	*	50 000	81 300	1.5
CH₃SH	80 900	110 000	188 300	2.0
(CH <sub>3</sub> ) <sub>2</sub> S	22 000	50 000	116 000	2.0
$(CH_3)_2S_2$	800	30 000	3 000	1.5
$C_{10}H_{16}$	1 900	*	*	0.1
CH₃OH	*	*	*	0.2
O <sub>2</sub>	*	*	*	9.0
NH <sub>3</sub>	*	*	*	*
H <sub>2</sub> O	20 000	330 000	*	6.0
CO <sub>2</sub>	*	*	*	*

#### Table 7-2. Examples of analyses of CNCG

\*) not analysed or below detection limit

Table 7-3. Examples of the heat values of the components of CNCG, BLRBAC

Component	kJ/kg(dry)
H <sub>2</sub> S	15 280
CH₃SH	26 100
(CH <sub>3</sub> ) <sub>2</sub> S	30 890
$(CH_3)_2S_2$	23 630
Turpentine	41 560
Methanol (gas)	22 720

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CNCG are usually not cooled or heated up in the same way as DNCG. An ejector or a liquid ring compressor is used to transfer CNCG. After these devices in the CNCG system are situated the droplet separator, valve group, flame arrester and rupture disc before incineration.

CNCG incineration and collection systems must be designed to confirm that leaks from the gas lines are impossible, that water cannot enter the furnace with the gases and that the risk of fire / explosion is minimised.

# 7.2 Starting / tripping logic for incineration of CNCG

It must be possible to supervise the incineration of CNCG in the recovery boiler and to control starting and stopping of the incineration of CNCG from the same main control room where other activities related to the operation of the recovery boiler are controlled.

The purpose of this section is to describe the process conditions to be fulfilled by the interlocking logic controlling the incineration of CNCG. The focus is on the most vital conditions that a safe automation system must fulfil. Because of differences in equipment design, process conditions and technical implementation, the interlocking logic of any CNCG burning will also include other conditions than those presented here.

This recommendation does not cover interlocking in the collection points of CNCG, though these are often partly implemented in the same system as interlocking related to incinerations.

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# 7.2.1 Starting logic for the CNCG incineration

The incineration of CNCG can be started when e.g. the conditions below are fulfilled, Table 7-4. Because of differences in commissioning year, equipment design, process conditions and technical implementation, the interlocking logic of any CNCG burning will also include other conditions than those presented here.

Table 7-4. To introduce CNCG to the recovery boiler, the following conditions should be fulfilled:

	Condition	Purpose of condition
1	Emergency shutdown not activated	Prevent CNCG feed when boiler is not in accepted condition
2	Boiler furnace heat loading is above 0.7 MW/m <sup>2</sup> . <b>This limit shall be defined on a case-by-case basis</b>	Confirm sufficiently stable furnace conditions to oxidise TRS compounds (temperature, retention time)
3	Burner support flame is on	Confirm sufficient incineration conditions in the burner
4	Flame scanner shows that there is flame in support fuel	Confirm flame on
5	Burner combustion air inlet pressure and flow above minimum	Confirm sufficient air flow to burner
6	Burner opening is not plugged (operator should check)	Confirm a safe CNCG incineration

# 7.2.2 Tripping logic for the CNCG incineration

The incineration of CNCG is interrupted for example if any of the conditions below is fulfilled, Table 7-5. Because of differences in commissioning year, equipment design, process conditions and technical implementation, the interlocking logic of any CNCG burning will also include other conditions than those presented here.

 Table 7-5. Any of the following conditions will divert CNCG from the recovery boiler:

 Condition

 Purpose of condition

	Condition	Fulpose of condition
1	Emergency shut-down activated	Prevent CNCG feed when boiler is not in accepted condition
2	Boiler furnace heat loading is below 0.7 MW/m <sup>2</sup> . This limit shall be defined on a case-by-case basis	Confirm sufficiently stable furnace conditions to oxidise TRS compounds (temperature, retention time)
3	High level in CNCG condensate draining system	Prevent water from entering the boiler
4	Pressure of CNCG before burner is below low limit	Prevent flame propagation backward in the pipeline (burn-back)

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# 7.2.3 Capacity limit

The incineration of CNCG requires sufficient temperature and retention time in the furnace to allow the gases to be combusted into carbon dioxide, water vapour and sulphur dioxide. A high enough temperature is achieved by raising the boiler load sufficiently and/or using support fuel. The minimum load as steam flow is determined by the equipment supplier. Because nominal load is often a somewhat obscure concept, it is recommended that this capacity should correspond to a furnace heat loading of at least 0.7 MW/m<sup>2</sup><sub>bottom</sub>. An example of how to calculate the furnace heat load is given in Appendix I.

It is recommended that the incineration of CNCG is interrupted if for example any of the following alarms is activated, Table 7-6:

	Table 7-6. CNCG alarms		
	Alarm	Purpose of alarm	
1	Boiler CO emission exceptionally high (over 1000 ppm for more than 1 min)	There is a noticeable disturbance in black liquor burning	
2	Boiler house hydrogen sulfide concentration alarm (H <sub>2</sub> S) is activated	Check if there is a leak in the CNCG system	
3	Black liquor dry solids drops below the alarm limit	Confirm a stable and safe burning	
4	Flame arrester pressure difference over upper limit	Flame arrester plugged/becoming plugged	
5	CNCG flow to burner drops below alarm limit (the flow is monitored by pressure)	Verify CNCG introduction to burner	

#### 7.2.4 Burner and use of support flame

CNCG can only be incinerated in an appropriately designed separate burner. The burner for CNCG shall be equipped with a separate air register and a separate lance for support/pilot fuel, which may be for example oil, gas, methanol, turpentine or tar oil. The use of DNCG as air in the burner of CNCG is not recommended because of their moisture and impurities.

The electrical and automation systems of the CNCG incinerator must meet the requirements for electrical and automation systems related to gas incineration. If oil is used as auxiliary fuel, the corresponding requirements for oil must be met.

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The incineration of CNCG requires a sufficiently high incineration zone temperature. In general, a temperature of 900 °C is required. The temperature requirement is met if CNCG are led below the liquor guns when the boiler operation is stable and boiler load sufficient. If CNCG are led above the liquor guns, attention must be paid to leading them to a place in the boiler where this temperature is exceeded. Another possibility is to use a support flame with sufficient capacity.

With small loads the purpose of the support flame is to ensure stable ignition and incineration of CNCG. The loading of the support flame shall be at least 10% of the maximum heat input of the burner. The support flame shall be supervised by a flame scanner.

The CNCG support fuel lance shall be equipped with local control panel from where support fuel burning is always started. The incineration of CNCG can then be started from the control room. Both of the above-mentioned operations can be stopped from the control room or from local control panel.

Figure 7-2 shows an example of a CNCG burner photographed from the outside and from the inside of furnace. The CNCG burner, methanol lance, flame scanners, flame arrester and support fuel lance are shown.





Figure 7-2. Inside and outside of a CNCG burner.

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When the boiler operates at a furnace heat loading of over  $0.7 \text{ MW/m}^2$ , two attempts can be made to ignite the support flame from the control room. However, this limit shall be defined on a case-by-case basis. The first ignition attempt shall always be made by using local control box.

When the support flame scanner doesn't detect flame, CNCG may be led to the recovery boiler for a while (for example 3 minutes) before shutting the quick-acting valves. During this time the start-up sequence for the alternative burning location can be started.

No support flame is needed when the following conditions apply, Table 7-7. The condition may vary depending on commissioning year, equipment design, process conditions, and technical implementation.

Table 7-7. Conditions for CNCG incineration without a support flameConditionPurpose of condition

 Boiler furnace heat loading is above 1.5 MW/m<sup>2</sup>. This limit shall be defined on a case-by-case basis Confirm sufficiently stable furnace conditions (temperature, retention time)

# 7.3 Pipeline system

The length of the pipeline system for CNCG inside the boiler house should be kept as short as possible. The pipelines should be installed with a view to avoiding critical locations, such as the dissolving tank and its environment, weak corners, emergency exits and stairways.

The pressure vessel and chemical handling legislation shall be taken into account in the design and installation of the pipeline system.

Pipelines should preferably be made of acid proof steel EN1.4436 (SS2343) or corresponding. Certain compounds in NCG, such as turpentine and methanol, are strong solvents, so the use of glass fibre and plastic parts is prohibited.

# 7.3.1 Steam purging of pipelines

When incineration is stopped, the pipelines for CNCG should be flushed from the shut-off valves to the boiler by purging them with an inert medium. In practice, the

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pipelines are always purged with steam. Purging with air is not recommended, because an explosive mixture is created at the interface between the purging air and the CNCG to be purged.

Steam purging implies a risk of water condensate in the lines reaching the furnace thus causing a dangerous situation. When designing the pipeline, attention should be paid to leading water possibly condensing in the pipeline to the condensate collection system.

# 7.3.2 Pipeline pressure measurements

The pipeline for CNCG shall be equipped with pressure gauges after the ejector and immediately ahead of the incinerator for CNCG. An alarm is activated if overpressure or minimum pressure is detected in the pipeline.

Plugging of the pipeline can be supervised based both on flow rate and pressure measurements.

# 7.3.3 Potential balancing

Potential balancing is carried out for CNCG lines. For instance in flanges, hatches and connections where a galvanic isolation may be formed, for example due to the isolation materials used, potential balancing must be performed. Potential balancing shall be made according to the given instructions and verified with a field log.

# 7.4 Transfer of CNCG

Fan is not allowed to use for the transfer of CNCG. Instead, the use of an ejector or liquid ring compressor is recommended. The temperature of the steam ejector and of the steam must not exceed 200  $^{\circ}$ C (corresponds to a steam pressure of approximately 12 bar(g)), because of the auto-ignition temperature of the gas components in CNCG gas.

If necessary, the CNCG ejector / liquid ring compressor can be placed inside the recovery boiler building.

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### 7.4.1 Pressure-control steam

Low pressure steam is used for controlling CNCG pressure before burner. The functioning of the steam lines drains must be monitored at all times to prevent water from entering the furnace.

### 7.4.2 Valves

The valves of the CNCG incineration system shall be selected with care. Special attention shall be paid to their sealing characteristics.

There should be two quick-acting valves in the inlet line for CNCG to the burner. Between them there should be a ventilation pipe with corresponding valve. The CNCG line shut-off valves should be equipped with "fail-close" actuator which will close CNCG introduction automatically if operating energy is turned off. The valve of the ventilation pipeline between the shut-off valves must open at the same time (fail-open). Valves must be provided with limit switches indicating position to the automation system.

It must be possible to close the pipelines for CNCG to the boiler house, also from outside the boiler house, with so-called emergency shut-off valves. The need for closing the pipelines from the outside arises from the fact that in a danger situation the CNCG flow inside the boiler house must be stopped.

The valves selected must comply with the corresponding regulations for inflammable gases, for example fire endurance. Recommended material for the valves is acid proof steel EN 1.4436 (SS2343) or equivalent.

# 7.4.3 Heating/cooling

Generally, the CNCG are not heated or cooled.

# 7.4.4 Droplet separator

A droplet separator should be used after ejector/liquid ring compressor to remove possible water droplets from the gas.

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# 7.4.5 Flame arrester

A flame arrester must be used for CNCG. The purpose of the flame arrester is to prevent flame propagation along the pipeline from the furnace towards the incoming CNCG.

If there is a system for cleaning the flame arrester installed, the cleaning pipelines must not be permanently connected. The pressure difference of the flame arrester must be measured and the flame arrester equipped with an alarm.

# 7.4.6 Underpressure protection

Underpressure protection by using air as make-up gas is not allowed for CNCG. It is recommended that pipelines and equipment be dimensioned so that no underpressure protection is needed.

# 7.4.7 Overpressure protection

Overpressure protection opening direct into the boiler house is not allowed for CNCG in the boiler building. The flow of CNCG caused by breaking of the overpressure protection shall be conducted to a point where it does not represent a hazard and where its negative impacts are minimised. Attention should be paid to draining of pipes with overpressure leading to outside to prevent freezing. Breaking of the overpressure protection must activate an alarm.

The most common type of overpressure protection is a rupture disc which activates an alarm.

# 7.4.8 Rupture discs

Piping section shall be equipped with rupture discs if a process upset condition or equipment malfunction could lead to pressure build up over the design pressure. This kind of pressure is for example the pressure generated by medium-pressure steam blowing. Breaking of the rupture disc must activate an alarm.

The recommended material for rupture discs is acid-proof steel or graphite.

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Rupture discs shall be installed in places where they will not represent a hazard to people working on the operating floors.

# 7.5 Condensate draining

Pipelines for CNCG shall be provided with condensate drains. The condensates contain large amounts of malodorous compounds. The condensates shall be collected into a pumping tank and pumped from there to foul condensate tank in the evaporation plant.

# 7.5.1 Size of condensate draining lines

Because of the risk of condensate overflow and plugging, the recommended minimum pipeline diameter for condensate drain connections and pipelines starting from these is 50 mm. Connections and condensate pipes installed outdoors shall be equipped with electric tracing if there is a risk of freezing.

# 7.5.2 Pipe slopes and locations of condensate drains

Pipelines must slope towards the condensate drains. The recommended slope for pipes, elsewhere than in the recovery boiler plant, when condensate travels in the direction of the gas flow is 1:100 and counter to the direction of the gas flow 1:25. Pipeline diameters shall be large enough to prevent flooding of condensates in the system.

Because of the risk of water entering the furnace, the aimed slope of pipes in the recovery boiler plant in the direction of the gas flow is 1:100 and counter to the direction of the gas flow 1:1 or more. In pipeline sections where the recommended slopes cannot be achieved, special care shall be taken in designing the condensate drainage system for the pipe in question.

When designing condensate draining systems attention should be paid to e.g. the size, amount and location of drains. The last condensate drain shall be placed so close to the recovery boiler that the length of the duct from this drain to the furnace is minimised. Special attention shall be paid to the condensate draining of pressure retaining steam lines.

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# 7.5.3 Water seals

To prevent CNCG from leaking via the condensate drains, the condensate lines must be equipped with water seals or a common condensate seal tank.

To confirm that the pressure generated by the ejector in the pipelines for CNCG will not rise so high that it causes the water seal to be emptied, the rated values of the ejector (overpressure and underpressure), as well as the process requirements (for example boiler system bottling) must be taken into account in the dimensioning of the water seal.

The water seal dimensions should be large enough so that the suction of the ejector does not drag droplets with it.

The water level in the water seal must be monitored. One solution is to lead a constant flow to the water seal, which is verified by flow measurements.

# 7.6 Alternative location

There shall be an alternative location / system where the gases can be diverted automatically if the incineration of CNCG in the recovery boiler is interrupted. There are multiple process equipment which can be considered as alternative location, for example power boiler, auxiliary boiler, flare, lime kiln and stack. The intention of diverting to an alternative location is to ensure low odour emissions.

The automatic valve used to divert CNCG from recovery boiler to the alternative location must be fail-open i.e. open automatically, if the supply of operating energy is turned off. Valve must be equipped with limit switches indicating position to the automation system.

# 7.6.1 Steam purging

It must be possible to steam-purge the pipeline of the alternative location / incineration system for CNCG.

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# 7.6.2 Location of flare

If the alternative outlet / incinerator for CNCG is a flare, it should preferably be located on the roof of the recovery boiler plant.

# 7.7 Concentration measurement

There is no need for continuous measurement of the concentrations of CNCG.

The Finnish Recovery Boiler Committee recommends that the concentrations of CNCG be measured at the point of origin, if equipment changes have been made at this point.

In addition, the Finnish Recovery Boiler Committee recommends that the content of sulphur and possibly also of oxygen to incineration be measured at least once a year.

# 8 METHANOL / TURPENTINE INCINERATION IN THE RECOVERY BOILER

In pulp mills, liquefied methanol / turpentine can be burnt in the recovery boiler, in the lime kiln, in a separate incinerator for NCG, in the power boiler and in a flare. If there is no backup incineration system, methanol/turpentine storage capacity corresponding to for example 24 hours' production must be available. Liquefied methanol and turpentine may be fired separately, or in a mixture. If turpentine is mixed to methanol, characteristics of these streams must be taken into consideration for example turpentine heat value is ~40 MJ/kg and methanol ~20 MJ/kg and turpentine's tendency to collect on top of the storage tanks due to poor solubility. Typically turpentine is led to the suction side of the methanol pump.

The methanol and turpentine storages must comply with applicable regulations for storing inflammable liquid chemicals. Tanks must not be placed in the boiler house.

#### 8.1 Starting / tripping logic of the methanol/turpentine incineration

The purpose of this section is to describe the process conditions to be fulfilled by the interlocking logic controlling the operation of the methanol and/or turpentine burner, in addition to those of a normal gas/oil burner. The focus is on the most essential conditions that a safe automation system must fulfil as a minimum. Because of differences in equipment design, process connections and technical implementation, the interlocking logic of any recovery boiler will also include other conditions than those presented here.

Methanol / turpentine can be used in CNCG burners as support fuel and as fuel in start-up burners. When using methanol / turpentine as fuel in the start-up burner, the temperature in the furnace must be sufficiently high. Methanol firing can be started earlier than the incineration of CNCG. In this case the interlocking conditions must be defined on a case-by-case basis.

To ensure safe and stable burning the methanol / turpentine quality (e.g. water content) must be monitored for example measuring methanol / turpentine density. Normal density of methanol is  $0.80 \text{ g/cm}^3$  and turpentine  $0.85 \text{ g/m}^3$ . If certain limit is exceeded, the stream must be diverted from the burner.

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It must be possible to supervise the burning of methanol and turpentine in the recovery boiler as well as to control starting and stopping methanol / turpentine burning from the same main control room where other activities related to the operation of the recovery boiler are controlled.

# 8.1.1 Starting logic for methanol and turpentine burning

Methanol and turpentine burning can be started in the recovery boiler when the following conditions are fulfilled, Table 8-1. Because of differences in commissioning year, equipment design, process conditions and technical implementation, the interlocking logic of any methanol/turpentine burning will also include other conditions than those presented here.

Table 8-1. To admit methanol / turpentine to the recovery boiler, the following conditions should be fulfilled:

Purpose of condition

#### Condition

	Condition	Purpose of condition
1	Fire signal in boiler	Prevent odour nuisances
2	Methanol/turpentine lance in place and connected	Confirm the right position of the methanol/turpentine lance
3	Methanol/turpentine pressure above minimum pressure (delay)	Confirm proper atomization of methanol
4	Burner air pressure above low air pressure limit	Confirm sufficient supply of incineration air to the burner
5	Pressure of atomising air sufficiently high	Confirm sufficient atomisation of methanol and prevent methanol from entering compressed air pipelines
6	Burner damper in ignition position	Confirm sufficient incineration air for ignition
7	Flame scanner shows flame (ignition delay)	Confirm that the fuel is burning
8	It has been checked that the burner opening is not plugged	Confirm a safety of methanol/turpentine burning
ç	Methanol/turpentine density below upper limit	Confirm that burner heat value does not drop too much (too much water)

#### 8.1.2 Tripping logic for methanol and turpentine incineration

Methanol and turpentine incineration is stopped if any of the following conditions is fulfilled, Table 8-2. Because of differences in commissioning year, equipment design, process conditions and technical implementation, the interlocking logic of any methanol/turpentine burning will also include other conditions than those presented here.

	boller:		
	Condition	Purpose of condition	
1	Fire signal is lost	Prevent odour nuisances	
2	Methanol/turpentine lance not in place	Confirm the right position of the methanol/turpentine lance	
3	Methanol/turpentine pressure below minimum pressure (delay)	Confirm sufficient supply of methanol/turpentine to the burner	
4	Burner air pressure drops below low air pressure limit	Confirm sufficient supply of incineration air to the burner	
5	Pressure of atomising air too low	Confirm sufficient atomisation of methanol and prevent methanol from entering compressed air pipelines	
6	Methanol/turpentine density rises above the upper limit	Confirm that burner heat value does not drop too much	
7	Flame scanner indicates no flame	Confirm that the fuel is burning	

# Table 8-2. Any of the following conditions will divert methanol / turpentine from the recovery boiler:

#### 8.2 Electrical and automation systems of the burner

The electrical and automation systems of the methanol/turpentine burner must fulfil the conditions for corresponding systems related to oil/gas burning.

The methanol and turpentine lance are purged with steam or air. There must be boiler fire signal condition on before purging can be started (start-up burners on).

#### 8.3 Valves

The valves for methanol and turpentine incineration systems shall be selected with care. The lines should have quick-acting shut-off valves with "fail-close" actuator which will close methanol/turpentine flow automatically if operating energy is turned off. Shut-off valves must be equipped with limit switches indicating shut-off to the automation system.

The valves selected must comply with the corresponding regulations for inflammable gases, for example fire endurance. Acid-proof stainless steel EN 1.4336 (SS2343), or corresponding, is recommended for the valve construction material. The valve sealing material shall be resistant to dissolution (methanol and turpentine are solvents). Special attention shall be paid to the selection of sealing material.

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# 9 ACTIONS IN SPECIAL SITUATIONS

This section deals with the actions to be taken in situations where the recovery boiler is not operating at stable load.

# 9.1 Actions during disturbances

The Finnish Recovery Boiler Committee recommends that the incineration of CNCG, DNCG, vent gases, methanol and turpentine in the recovery boiler shall be stopped and they should be diverted to the backup incineration system in connection with any major disturbance situation at the recovery boiler.

If the boiler main interlock is initiated, the incineration of methanol, turpentine, dissolving and mixing tank vent gases, CNCG and DNCG in the recovery boiler shall be stopped.

If there is a risk of explosion or fire the import of methanol, turpentine, dissolving and mixing tank vent gases, CNCG and DNCG in the recovery boiler building shall be stopped. Therefore it is not recommended to continue flow of CNCG through boiler house to back-up incinerators.

# 9.2 Actions during shut-downs

During a shut-down, the incineration of NCG in the recovery boiler is recommended to be stopped when approaching interlocking limits (see tables 5.5, 6.3 and 7.5.) and gases are diverted to alternative location. When the incineration of CNCG is stopped, the pipeline – from shut-off valves to the boiler – shall be purged with steam and when the incineration of DNCG is stopped, the ducts are recommended to be flushed with air. If possible, the collection of DNCG should be operated during shut-downs.

# 9.3 Actions during start-ups

NCG handling systems should preferably be kept in operation also during shutdowns. If there has been a stop in the incineration of NCG in the recovery boiler, the following items must be checked before the NCG system is started up again:

 that any maintenance or repair work done during the shut-down is completed and that NCG equipment is no longer being serviced/maintained

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- that the equipment and pipelines subject to maintenance or repair have been appropriately installed and cleaned of any debris
- that the valves connected to equipment and pipelines subject to maintenance or repair are in correct conditions and position for start-up
- that the equipment and pipelines subject to maintenance or repair are ready for use and tightly sealed. The tightness must be checked by test runs.

Before start-up, all DNCG lines that were out of use during the shut-down have to be ventilated and CNCG lines purged with steam and, if necessary, with nitrogen. The purpose of ventilation is to confirm that any NCG that have leaked into or condensed inside ducts and other equipment will not cause harm or risk situations.

Before start-up, all condensate tanks must be checked for overflows or drying-out.

Before start-up, all water seal fresh water flows must be checked to prevent water seals from drying out.

After start-up, when equipment, piping and connection flanges are warmed up to process temperature, it is good to check once again the tightening of bolts. Check also that groundings are connected.

#### 9.4 Actions during outage

During outages, NCG must be prevented from leaking into the boiler building. The purpose of separating NCG lines is to prevent gases from leaking into and accumulating within ducts and pipelines inside the boiler building during outages.

#### 9.4.1 Instructions for preparing NCG system for shut-down or maintenance

NCG lines, in the same way as other lines in the recovery area, must be made safe before any work is started. CNCG lines require steam purging and, if necessary, purging with nitrogen. When the incineration of DNCG is stopped, the gas ducts are recommended to be flushed with air. If shut-down or maintenance works are to be done in NCG systems, the relevant parts and equipment of the system must first be separated from the rest of the system and the separated equipment then effectively ventilated at the very beginning of the shut-down. Ventilation streams

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shall always be discharged into the atmosphere. NCG lines require also LEL and sulphur-containing gas measurement before starting work.

Flushing of CNCG lines is recommended to be done 24 hours before concentration measurement and the start of service/maintenance work on CNCG lines. Flushing of DNCG ducts is recommended to be done eight hours before concentration measurement and the start of service/maintenance work on DNCG ducts.

Before starting work, a risk assessment shall be made in which especially all pipelines coming to the working area are mapped. A written work permit practice before starting work is recommended for example working inside NCG devices always needs written work permits.

# 9.4.2 Instructions for maintenance work during outages

Welding generates sparks inside the NCG system and therefore involves an explosion risk. Maintenance work involving the NCG system always requires a special permit. In connection with an outage, the maintenance staff shall be told which lines are NCG lines and how repair and maintenance work shall be carried out on these lines.

# **10 SPECIAL INSTRUCTIONS FOR THE DESIGN OF NCG LINES**

These instructions have been prepared for designers of NCG lines. Because NCG lines are subjected to explosive, dissolving and corrosive compounds, design practices and materials shall be selected to meet specific design criteria for NCG pipelines / ducts, in addition to the criteria for normal ducts.

NCG ducts shall be resistant to mechanical, chemical and thermal impacts caused by their contents and ambient conditions (snow, ice, vibrations, hot and cold surfaces). Pipeline connection methods shall be adapted to the material used.

#### 10.1 Classification

NCG lines are subject to the stipulations of relevant chemical legislation. These lines are divided into different classes, depending on their toxicity.

The division of NCG into DNCG, vents and CNCG is not sufficient to characterise the hazardousness of the contents. Gas mixtures must be classified in accordance with regulation 807 (of the 26 of September, 2001) of the Finnish Ministry of Social Affairs and Health concerning classification criteria and labelling of chemicals. On this basis, each NCG line must be classified in accordance with the specific contents of the line in question.

If no other specifications are given, CNCG, methanol and turpentine lines can be designed preliminarily in accordance with the classification "toxic and inflammable".

If no other specifications are given, a DNCG line can be designed preliminarily in accordance with the classification "hazardous".

However, these classifications must be confirmed.

#### 10.2 Signs

NCG incineration equipment and pipelines shall be provided with appropriate markings. Markings shall always include the texts "Concentrated non-condensible gases", "Turpentine", "Methanol" and "Dilute non-condensible gases", and whenever necessary, "Inflammable", "Toxic" and "Must not be welded or cut

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without supervision", and "Equipment must not be dismantled without permission in writing". In addition, all pipelines/ducts shall be provided with markings showing the direction of flow.

Smoking and the use of open fire are prohibited in areas were NCG are handled. Appropriate warning signs must be set up.

# **10.3** Condensate draining

In the design of condensate drain systems, special attention shall be paid for example to the size, amount and location of drains. See chapters: 5.10, 6.11 and 7.5.

# **10.4 Duct/pipeline material**

Recommended material for DNCG ducts is corrosion-resisting steel EN 1.4301 (SS2333) or equivalent.

Pipe PN  $\geq$  10 shall be used for CNCG. Recommended material for pipelines is acid-proof steel 1.4436 (SS2343) or equivalent.

Recommended material for pipelines for incineration of methanol/turpentine is EN 1.4436 (SS2343) or equivalent.

Some NCG compounds, such as turpentine and methanol, are strong solvents, so the use of plastic or glass fibre parts is prohibited.

# **10.5** Duct pipeline insulation

NCG contain large amounts of water and other condensing substances. Condensation and the handling of condensates shall be minimised. NCG lines shall be insulated in places where their surface temperature is high.

Drains shall be insulated and outdoor drains shall, if necessary, be provided with heat tracing.

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# 10.6 Pipe / duct slopes

Almost without exception, NCG contain significant amounts of water vapour. Even if ducts are carefully insulated and/or provided with heat tracing, there is always a possibility of condensation. The slope instructions and locations of condensate draining connections are described in more detail in the following chapters: 5.10.2, 6.11.2 and 7.5.2.

# 10.7 Valves / dampers

Valves/dampers for NCG incineration systems shall be selected based on the characteristics of the gas.

EN 1.4301 (SS2333) or corresponding is the recommended material for DNCG valves/dampers.

Stainless steel EN 1.4436 (SS2343) or corresponding is the recommended construction material for valves for CNCG.

Stainless steel EN 1.4436 (SS2343) or corresponding is the recommended construction material for valves of methanol/turpentine incineration systems. The valve sealing material must be resistant to dissolution (methanol and turpentine are solvents).

# **10.8** Flanges, connections

Special attention shall be paid to effective sealing of flanges and connections under any conditions. When replacing seals, special care shall be taken to select the right kind of sealing material.

Connections shall retain their good sealing properties also in use (oxidation, reactions with sulphur compounds contained in NCG, freezing, bending, etc.).

# **10.9 Fans**

Fans are recommended for transferring DNCG and vent gases.

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# 10.10 Ejectors / liquid ring compressor

A fan must not be used for transferring CNCG. Instead, a steam ejector or a liquid ring compressor shall be used. The maximum allowed steam temperature of the steam ejector is 200 °C (corresponding to a steam pressure of approximately 12 bar(g)) because of the auto-ignition temperature of the gas components. In connection with a disturbance or start-up situation, the CNCG may contain so much oxygen that the gas mixture is ignitable.

# **10.11 Duct / pipe sizing**

When incinerating CNCG, operating gas velocities should exceed the flame propagation velocity under all circumstances.

The operating pressure of CNCG pipes is -10...+10 kPa and that of DNCG ducts -5...+10 kPa.

DNCG ducts must withstand underpressure up to 10 kPa. CNCG pipes must withstand full underpressure (100 kPa).

CNCG are typically classified as extremely toxic, or inflammable. The pipelines for such substances shall be sized in accordance with the operating pressure, with a minimum design pressure of 4 bar(g). A pressure of 1.3 times the design pressure is enough for sizing valves and other pipeline auxiliary equipment. The pressure of the purging steam shall be taken into account in selecting the design pressure.

DNCG are typically classified as harmful. The design pressure of a pipeline for harmful NCG shall be at least 1.3 times the operating pressure, with a minimum of +10 kPa(g).

#### **10.12** Location of flame arrester

The flame arrester should be installed as close to the actual burner as possible. If the bottom of the flame arrester is below the bottom level of the pipeline, the flame arrester must be provided with a condensate drain.

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# **10.13 Location of rupture discs**

Rupture discs shall be installed in places where they will not represent a hazard to people working on normal operating floors. Their condition shall be monitored in the automation system by activating an alarm.

Rupture discs should be installed as a direct continuation of the duct section in question, without bends. The duct continues by means of a t-branch.

#### **10.14** Location of bypass

A bypass duct / pipe outlet shall be installed as high as possible. The bypass is recommended to be taken as a separate pipeline to the stack or the roof of the recovery boiler plant.

The automatic valves for bypass duct must have fail-open actuators i.e. open automatically, if the supply of operating energy is turned off. This will confirm that gases will be led always to safe place even in case there is no instrument air available. Valves must be provided with limit switches indicating position to the automation system.

#### **10.15 Hazardous area classification**

The classification of different places where NCG equipment is located is based on the instructions and stipulations in the legislation on chemicals.

For CNCG and turpentine-containing foul condensates, the Hazardous area classification often has to be based on the classification of places involving a risk of explosion. Turpentine is lighter than water and poorly soluble, so in case leakage it separates to water surface and evaporates to the air.

Hazardous area classification and impact areas are also defined for possible leakage points. Equipment that will be situated in the impact area of a specific place class will be designed from components in conformity with the classification. Zone 1 means that explosive gas will occur sporadically and Zone 2 that gas is not expected to occur in the area in question during normal operation.

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If a place is considered risk-prone, it can be equipped with automatic high efficiency ventilation in case that the  $H_2S$  concentration rises too much.

The boiler house and the possible area in the immediate vicinity of the CNCG, methanol and turpentine burner shall be equipped with a measuring device that will activate an alarm if the hydrogen sulphide ( $H_2S$ ) or VOC concentration becomes too high.

# **10.16 Manufacturing permits**

A manufacturer making pipelines whose operating pressure exceeds 0.5 bar(g) and which conduct inflammable gases (usually CNCG) must have a manufacturing permit as stipulated in the pressure vessel legislation, and also an officially appointed manufacturing supervisor.

If DNCG, because of their contents, are classified as harmful substances, the pipeline manufacturer does not need a manufacturing permit or manufacturing supervisor as stipulated in the pressure vessel legislation.

Installation works related to methanol and turpentine lines shall be carried out in accordance with relevant regulations (gas installations, oil installations, and pressure vessel manufacture). In practice, it is advisable to handle the installation in the same way as installation of oil and gas pipelines for recovery boiler start-up burners.

In all works related to manufacture and installation, it is recommended to use companies with relevant documentation proving their competence.

Installation works for the burner and support fuel pipelines can only be carried out by a company holding the relevant installation permits.

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# 11 OTHER INSTRUCTIONS AND REGULATIONS AFFECTING DESIGN

# 11.1 Finnish law

The most important Finnish laws and regulations concerning NCG are:

- Chemicals Act (744/1989)
- Decree on the Industrial Handling and Storing of Dangerous Chemicals (59/1999)
- Decree of the Ministry of Social Affairs and Health on Chemicals referred to in Annex VI to the CLP regulation (5/2010)

# 11.1.1 Hazard and operability study (HAZOP)

The Chemicals Act defines hazardous gases and requires a hazard and operability study (e.g. HAZOP) to be carried out for NCG.

# **11.1.2** Classification of pipelines

The Chemicals Act and the Decree on the Industrial Handling and Storing of Dangerous Chemicals specify technical equipment requirements and stipulate, in practice, for example how pipes are to be classified, how regular inspections are to be carried out and that CNCG are to be transferred with an ejector and not with a fan.

At present, there are two parallel legislations in force concerning the classification, labelling and packaging of chemicals. The classification and labelling regulations according to the so-called Substance Directive (67/548/EEC) and Mixture Directive (1999/45/EC) are still in force and they have been enforced in the Chemicals Act (744/1989), Chemicals Decree (675/1993), as well as in the Ministry of Social Affairs and Health Decree on Chemical Classification Principles and Labelling (807/2001) (the so-called outgoing system).

EU's new Regulation on Classification, Labelling and Packaging of Substances and Mixtures, the so-called CLP Regulation (EU) no. 1272/2008 entered into force on January 20, 2009. This regulation is as such in force in all EU member states. The outgoing legislation is in force within certain transition periods.

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The Ministry of Social Affairs and Health Decree on Chemical Classification Principles and Labelling (September 26, 2001/807) provides a formula for determining inflammability, using standard ISO 10156, Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets, and its Tables 1 and 2. DNCG are classified as harmful gases but not as explosive gases.

Systems for separate incineration of CNCG are, in practice, constructed in accordance with the requirements for natural gas equipment. There are detailed instructions for natural gas, which specify accurate requirements for example for valves and flushing systems.

# 11.1.3 Classification of potentially explosive atmospheres (ATEX)

The EU ATEX Directive (94/9/EU) refers to potentially explosive atmospheres. In addition, instructions concerning potentially explosive atmosphere classification are given in standard EN 60079-10: 1956, which has been translated into Finnish and published as SFS Manual no. 59 (4th edition 1998). The classification of potentially explosive atmospheres is applied to CNCG. The zones and their impact areas are defined for possible leakage points. Equipment to be situated in the impact area of the zone class in question is designed with components in conformity with zone class. Zone 1 refers to a place in which an explosive atmosphere is likely to occur in normal operation occasionally and Zone 2 to a place in which an explosive atmosphere is not likely to occur in normal operation.

# **11.2 European standards**

The European standard on pressure vessels (EN 12952-8, Annex A.3.3.) imposes certain restrictions on the incineration of NCG in a recovery boiler. CNCG can be incinerated in a recovery boiler, provided that the steam generation is at least 50% of the boiler's nominal load with black liquor.

In addition, the standard requires precautions to be taken in order to prevent aqueous solutions from penetrating into the boiler furnace together with gases or fuel, and to prevent CNCG from escaping into the boiler house's indoor atmosphere. The above-mentioned clause does not apply to DNCG.

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All NCG lines must be equipped with automatic shut-off valves.

## **11.3 Existing instructions**

Sweden's Sodahuskommittén and the American BLRBAC have issued instructions for the handling and incineration on NCG. BLRBAC's instructions are very detailed and include accurate technical descriptions of design solutions.

# 11.3.1 Sodahuskommittén

Our Swedish sister organisation, Sodahuskommittén, published in December 2008 a decision that their recommendation from then on will be published only in Swedish and they are intended for the sole use of the members only.

# 11.3.2 BLRBAC

BLRBAC has issued instructions for minimising risk situations, entitled "Recommended good practice for the thermal oxidation of waste streams in a black liquor recovery boiler", updated in February 2012.

The document lists inflammable NCG and defines their explosion limits. It explains where NCG are collected and how they can be destroyed, giving instructions on how to incinerate methanol and turpentine, among others. A whole chapter is dedicated to the handling of chip silo vents. The document defines the conditions at which black liquor solids contents NCG can be incinerated safely.

In a problem situation, and especially in practice when the Emergency Shutdown Procedure (ESP) is activated, NCG shall be instantly diverted from the recovery boiler in the same way as other fuels.

BLRBAC's document also warns of the toxicity of NCG and the risk of corrosion that they involve, in spite of the fact that there is no proven evidence of corrosion of pressure vessels caused by NCG.

The document is very comprehensive, including also conditions for interlocks and examples of the PI and interlocking diagrams of incineration and collection systems.

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## 12 DEVIATIONS FROM PRACTICES DESCRIBED IN OTHER INSTRUCTIONS

The Finnish Recovery Boiler Committee has endeavoured to comply with other countries' recommendations and instructions concerning incineration of NCG in the recovery boiler. At least the following factors deviate from those presented in other recommendations.

## 12.1 Deviations compared to BLRBAC's instructions

The Finnish Recovery Boiler Committee's instructions differ from those of BLRBAC (http://www.blrbac.org/) for example in the following respects:

- Chapter dedicated to the handling and incineration of chip silo vents
- Chapter dedicated to the handling and incineration of stripper off gases (SOG)
- Examples of the PI and interlocking diagrams of incineration and collection systems
- The recommendation for relative humidity of DNCG and vents after condensers 50%, corresponding to a temperature of < 43.3 °C (110 °F). Heating at least 22.2 °C (40 °F) above condensation temperature.</li>
- The incineration of DNCG can be started when the steam flow greater than 30% of the steam flow at MCR.
- The incineration of CNCG can be started when the steam flow greater than 50% of the steam flow at MCR
- Incineration of methanol/turpentine/soap/tall oil mixed with black liquor.

#### **13 EXAMPLES OF ACCIDENTS**

The NCG system may involve an explosion risk if the gas concentration is within the explosion range. The gas concentration has either to be kept high enough or low enough. Especially shut-down and start-up situations are challenging. Generally, explosions in recovery boilers related to NCG have been caused by DNCG systems.

In the following, a number of examples of damage and risk situations known to the Finnish Recovery Boiler Committee are described. The damages are described to give the reader of this recommendation a concrete picture of possible danger situations related to the collection or incineration of NCG. Similar events have also been recorded in other mills.

#### **13.1 Example 1:**

An explosion in the mill concrete stack damaged the DNCG steel stack across its whole length, a part of the combustion gas stack of the lime kiln and a part of the CNCG pipeline. The explosion was the result of several interacting factors. The operation conditions preceding the explosion increased the concentration of the gas mix in the bypass stack to ignition and explosion concentration. The prevailing weather conditions forced the hot combustion gases from the lime kiln into the outgoing DNCG causing ignition.

#### Causes:

- DNCG of the evaporation plant had reached explosion concentration during normal operation and shut-down.
- Gases from the firing liquor tank were led to the collection system of DNCG.
   There was heavy gas formation from the firing liquor tank 22 hours before the explosion.
- Fibre line DNCG fan was stopped and therefore there was no dilutive effect from the DNCG in the fibre lines.
- Because of the prevailing weather conditions the hot combustion gases (approximately 260 °C) from the lime kiln were directly mixed with the

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outgoing DNCG which were above the lower explosion limit. The bypass stack of the DNCG and lime kiln combustion gas stack were at the same level.

# Measures taken after the explosion

- The fan of the DNCG in the fibre lines shall be kept in operation during shutdowns while simultaneously conducting dilution air to the suction side of the fan to ensure a low enough concentration.
- The gases from the firing liquor tank shall be conducted to the collection system of CNCG or evaporators, not to the collection system for DNCG.
- The temperature and solid content of the liquor in the firing liquor tank shall be decreased to 117 °C respectively 67-69% for the shut-down to prevent gas formation reactions.
- The circulation pump of the DNCG scrubber shall be kept in operation during outages.
- Clear instructions shall be given for the operation of DNCG during outages.
- Circulation water from evaporation NCG scrubber shall not be pumped from to the spill liquor tank, from where the gases are sucked back into the DNCG collection system

## **Other recommendations**

- The concentrations of methanol, TRS compounds and turpentine in DNCG, liquors and condensates shall be identified.
- A concentration measurement or flow measurement shall be installed in the DNCG collection system for monitoring.
- A simulation programme shall be made to specify in a reliable way the amount of dilution air in different operation situations.
- The capacity of the fan for the DNCG in the evaporation plant shall be increased and the suction side equipped with an intake for dilution air.
- The lower part of the bypass pipe for DNCG shall be redesigned.
- The use of the fan shall be stopped and the gases conducted to their own pipe on the suction side, if DNCG reach explosion concentration.
- A hazard and operability study (HAZOP) shall be made of DNCG concentration under normal operation and in shut-down situations.



# **13.2 Example 2:**

An explosion happened in the DNCG duct close to the NCG boiler.

#### Causes:

The chip feeding system to the digester stopped due to problems with the black liquor filters during mill start-up. Thereafter the chip bin level was raised to 95% and the chips were presteamed with fresh steam, generating a surface temperature of 90  $^{\circ}$ C in the chip silo.

Half an hour after the shut-down, chip feeding to the digester was restarted and flash steam was led to the chip silo, because the CNCG system could not keep sufficient underpressure in the collection line to the CNCG burner. The presteamed chip bed was unable to condensate and to absorb the steam which therefore passed through the chip bed, quickly increasing the temperature of the upper part of the chip silo, and further to the DNCG collection system.

The temperature interlock after the chip silo vent condensers reached the interlock limit of > 55 °C and the gases were diverted to the bypass pipeline. Before this safety interlocking, gases got into the collection system of DNCG for approximately 40 seconds, causing an explosion about 1.5 minutes after the flash steam valve was opened. The explosion occurred close to the NCG boiler burner in the collection pipeline.

## Measures taken after the explosion

Before starting up the mill again, the following measures were taken:

- The opening speed of the flash steam valve was slowed down (5%/min in range 0-10%), so that the amount of flash steam is controlled at start-up.
- The chip conveyor to the silo must be in operation at least five minutes before the flash steam valve to the chip silo can be opened, to control that there are fresh chips in the silo to condensate the flash steam.
- When the chip silo temperature rises above 90 °C, the cooling water valve of the condenser opens immediately 100%.

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# **13.3 Example 3:**

A fire was started in the DNCG duct damaging the front wall of the recovery boiler and approximately 2 m of the duct during boiler start-up.

## Causes:

The fire was possibly started by boiler backfire igniting the deposit accumulated at the bottom of the DNCG duct. The deposit formed at the bottom of the DNCG duct normally originates from the tall oil plant.

## Measures taken after the explosion:

- The DNCG fan was renewed.
- The preheating of air was intensified by adding a heat exchanger for fresh air, thus raising the temperature of the DNCG.
- The capacity of the collection system was increased.
- Interlocking related to incineration was checked.
- Dissolving tank vent gases were included in incineration together with DNCG.

## **Recommendations:**

Following matters that should be taken into account after the accident:

- The functioning of the scrubbers shall be improved to ensure a good scrubbing result. The liquid distribution, drop separation and temperature after the scrubber shall be checked for each scrubber.
- The control of the dilution of the DNCG system shall be checked.
- There should be a droplet separator ahead of the preheater.
- The composition of NCG shall be checked regularly according to incineration performance.
- Ducts shall be regularly checked and cleaned.
- A hazard and operability study (HAZOP) shall always be made when NCG system is modified together with the supplier of the NCG system.



#### **13.4 Example 4:**

Two explosions related to NCG are presented here. The first happened in the recovery boiler DNCG duct and the second in a pressurised firing liquor tank.

#### Causes:

When flash steam was conducted to the chip silo during a shut-down, CNCG were discharged into the collection system for DNCG through the chip bed or concentrated methanol in the chip bed was released. There was no condensation for the flash steam so it had to be led to the chip silo. The explosion took place in the recovery boiler's DNCG duct. The amount of recovery boiler secondary air had been manually reduced.

The second accident occurred in the pressurised firing liquor tank, which exploded when its circulation pump was left functioning during shut-down and a heavy formation of NCG compounds started inside the tank. There was no relief valve in the tank and it was not connected to the collection system for CNCG.

## Measures taken after the explosion

As a result of the explosion of CNCG in the chip silo's DNCG collection system, the mill invested in a reboiler where the chips are presteamed with clean steam. This improvement in the cooking plant eliminated the problems related to the collection and handling system for DNCG. The use of reboiler steam in the chip silo keeps the concentration of DNCG at a permanently low level. The acquisition of a backup incineration system was also considered because of odour problems, but the new reboiler solved the worst problem of the odorous gas source and the investment was abandoned.

The firing liquor tanks were connected to the CNCG collection system and a relief valve was installed in the tanks.

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# **13.5 Example 5:**

During start-up of the mill turpentine and NCG compounds with a concentration within the explosion limit escaped from the chip silo and started to burn explosively in the flare. The fire front advanced backwards to the DNCG fan, where a second explosion occurred.

#### Causes:

The explosion was the result of several interrelated factors in the chip silo, where the DNCG safety system was unable to control the exceptional conditions. The safety system functioned well under normal operation conditions, but was insufficient under exceptional conditions with partially unknown effects. As to the other tanks within the collection system, the changes in the DNCG are slower and the mill's safety systems have been enough.

The separate circumstances leading to the explosion are as follows:

- Long chip presteaming time in the chip silo (low-pressure feeder stuck)
- High concentrations of TRS and VOC in the chip silo and its gases at start-up
- Delay in the temperature measurement in the vent line from the chip silo
- Delay in the LEL analyser
- The NCG scrubber primarily condensates water vapour, resulting in an increased amount of NCG in the air volume. The LEL analyser was positioned ahead of the condensing process, resulting in a lower measured concentration.
- Operating failure of the dilution valve located on the suction side of the collection fan for DNCG.
- Automatic reopening of the collection valve for digester DNCG based on the measurement of the LEL analyser.
- Oriface plate in the vent pipe of the DNCG of the digestion plant.
- Flare flame out.

The amount of dilution air has been sufficient under normal operating conditions. The results are based on the measurements carried out in 1998 and 2000. However, the measurements do not cover exceptional conditions. The amount of dilution air is increased at three points in the DNCG collection and handling system:

- The underpressure of the DNCG fan via the chip silo and vent pipe of other tanks sucks dilution air at different collection points. The system, however, does not function if the system is pressurised and gas leaks out of it. In the case of the chip silo, a oriface plate has been installed in the dilution air outlet.
- The LEL non-condensible gas analyser opens the dilution value on the suction side of the NCG gas fan, if the concentration rises over 30% above the LEL limit.
- DNCG are led to the flare, where the necessary amount of additional air dilutes the non-condensible gas.

## Measures taken after the explosion:

- The operation mode of the chip silo and its control are developed.
- Modifications the NCG handling system and the related security systems are examined as a whole.
- A sufficient supply of dilution air under exceptional conditions is ensured.
- A safety system is built up according to safety automation principles.
- The follow-up of DNCG concentrations is improved and interlocking limits checked (development and location and possible duplication of the analyser).
- Exceptional situations are recognised and instructions for such cases are worked out.
- Dangers are systematically identified and risks assessed.
- Supervision is harmonised.

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#### **13.6 Example 6:**

Explosion happened in the recovery boiler tertiary air system. The DNCG duct and equipment (fan, heat exchangers, air nozzles etc.) inside recovery boiler building was damaged and replaced.

#### Causes:

There were disturbances in the chip silo due to stopping of the chip conveyor and leakage of flash steam into the silo vent gas system. The vent gases of the chip silo were connected to the DNCG collection system through the white liquor scrubber after the start-up of the mill. The connection was made because the chip silo was the primary individual odour nuisance at the mill. During the disturbance, the amount and concentration of chip silo vents strongly increased and combustible gas containing turpentine, methanol and TRS compounds got into the recovery boiler tertiary air system.

NCG measurements after the explosion showed that exhaust gas from the chip silo had exceeded the lower explosion limit concentration, and the gas could have ignited by backfire from the recovery boiler or by a spark from the fan.

Luckily, the explosion did not cause any personal injuries.

## Measures taken after the explosion

In the investigation report it was recommended that the exhaust gases from the chip silo shouldn't be taken to the DNCG collection system. The report, however, pointed out that if the vents are taken there for odour reasons, the vent line of the chip silo has to be equipped with turpentine condenser and scrubber where the gases are cooled down with cold water. Moreover, measurement of the lower explosion limit and bypass in danger situations were recommended.

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# **13.7 Example 7:**

Explosion happened in the recovery boiler DNCG system.

#### Causes

The concentration of the gas mixture in the DNCG incineration system had risen too high during the start-up phase following a shut-down of the pulp mill.

The gas mixture, whose concentration probably was within the explosion range, had escaped via a partly open shut-off valve and / or a water drain pipeline to the DNCG nozzles at the back wall of the recovery boiler's tertiary level during the start-up phase following a shut-down of the pulp mill. The mixture was ignited at the nozzles and the flame then propagated along the DNCG ducts to the front part of a heat exchanger, where an explosion occurred.

At present, mill keeps the NCG collection system running also during outages.

#### **13.8 Example 8:**

If water condenses in a DNCG line, there is a risk of smelt-water explosion, if the water gets into the recovery boiler.

Special attention should be paid to water drains which shall cover all lines comprehensively. The bypass stack should be situated as close to the boiler as possible in order to minimise the length of the line between the bypass stack and the recovery boiler building. For practical reasons, the bypass stack is situated close to the recovery boiler, because the ejector is often installed inside the recovery boiler building or in its vicinity, and the stack is always on the pressure side, after the ejector.

A serious explosion occurred at the mill because a relatively large amount of water entered the furnace via the CNCG gas burner. As a result of the explosion, four persons died and 13 were injured. Another smaller smelt-water explosion occurred 15 minutes later.

The ultimate reason for the explosions was probably the water that entered the furnace, putting out the fire on the char bed. The water apparently entered the

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recovery boiler through the CNCG burner, when the automation system switched off the combustion system, purging the gas line with steam, while at the same time flushing the condensed water in the line into the furnace.

#### **13.9 Example 9:**

The risk of poisoning by NCG needs to be pointed out to all those working with or close to NCG lines.

There was an accident where two members of the recovery boiler's operating crew were poisoned by non-condensible gases. The accident occurred when black liquor stopped flowing into the black liquor mixing tank as a result of plugging of the vent pipe. The mixing tank's level indicator was a pressure transmitter, and because of the increased pressure the transmitter's level indication was wrong. In a normal situation, residual liquor was conducted to the bottom of the mixing tank, about 2 m below the liquor surface, thus preventing hydrogen sulphide from spreading into the room.

In the accident situation, the liquor level dropped too much, and the residual liquor then caused a reaction releasing hydrogen sulphide. The gas pressure generated by the reaction closed the incoming black liquor valve, causing the formation of hydrogen sulphide to increase strongly. An operating crew member who was cleaning the vent gas line inhaled hydrogen sulphide coming from the opening. The person in question felt dizzy and went outdoors, after which he temporarily lost consciousness. Another member of the operating crew went to inspect the operation of the mixing tank, noting that black liquor-containing foam was streaming out from the inspection hatch of the mixing tank. He too felt dizzy, and went to the control room, where he informed the control room operator about the situation and then temporarily lost consciousness. The persons concerned had a check-up at the hospital and did not suffer any permanent injury. After this accident, the pumping of extra residual liquor to the mixing tank was stopped to eliminate the risk factors involved.

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# 14 CLOSING WORDS

The members of the Finnish Recovery Boiler Committee have called for a clear stand on the collection and incineration of NCG in chemical pulp mills. The reason for this is the general concern over safety and the functionality of the overall process.

Depending on their ignition or explosion range, NCG are divided into dilute gases, whose concentration is below the explosion range, and concentrated gases, whose concentration is above the explosion range.

The incineration of CNCG in the recovery boiler started attracting strong interest during the 1990s. DNCG have been incinerated in the recovery boiler before.

There have been numerous problems with the incineration of dilute and CNCG. Incineration involves certain risks, in the same way as incinerating other combustion gases, which is why a recommendation is needed. There are also different schools of thought, which has caused confusion and a lively debate on this subject.

There are numerous instructions for recovery boiler operation. The incineration of NCG requires a recommendation of its own to confirm safe incineration of NCG in the recovery boiler. The relevant legislation does not deal with NCG to any major extent; it is primarily governed by the general principles of the Chemicals Act. The purpose of this recommendation is to allow safe incineration of NCG in the recovery boiler.

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**APPENDIX I** Example of how to calculate furnace load

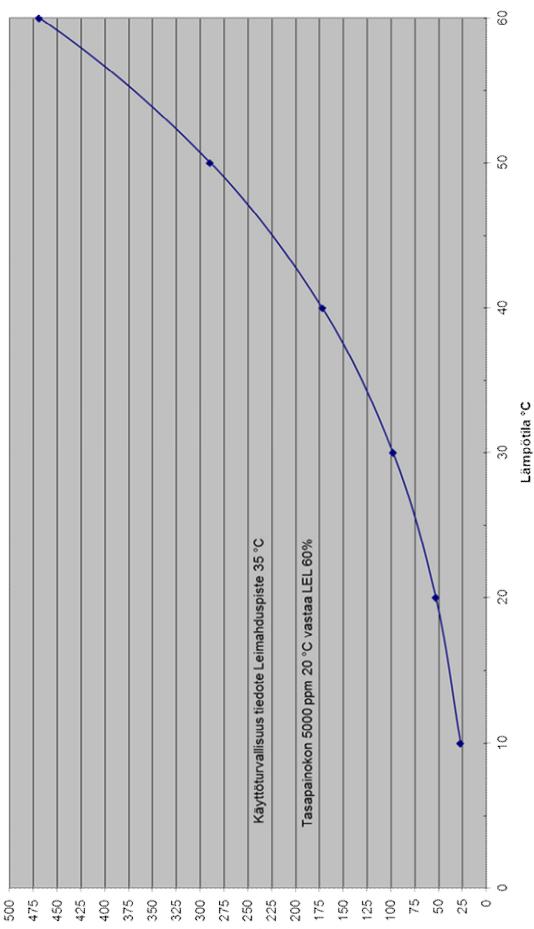
#### EXAMPLE OF HOW TO CALCULATE FURNACE LOAD

To confirm a standard procedure for calculating the minimum load for incineration, two ways to calculate the minimum load are presented in the following. In the first, the load is tied to the steam flow, in the second to the liquor flow. The unit for furnace heat loading is the net heat to steam generation divided by the floor area of the furnace.

	100	%	43	%
Boiler floor area	100	m <sup>2</sup>	100	m <sup>2</sup>
Steam generation	80	kg/s	34.3	kg/s
HP steam pressure	80	bar	80	bar
HP steam temperature	480	°C	480	°C
HP steam enthalpy	3349.5	kJ/kg	3349.5	kJ/kg
Feedwater pressure	100	bar	100	bar
Feedwater temperature	115	°C	115	°C
Feedwater enthalpy	489.6	kJ/kg	489.6	kJ/kg
Steam drum pressure	90	bar	90	bar
Sootblowing steam enthalpy	2942.9	kJ/kg	2942.9	kJ/kg
Blow-out enthalpy	1363.7	kJ/kg	1363.7	kJ/kg
Blow-out	1.5	%	1.5	%
Sootblowing	2.0	%	2.0	%
Heat to steam	2.922	MJ/kg	2.922	MJ/kg
	233.8	MW	100.2	MW
Net heat per floor area (furnace heat loading)	2.34	MW/m <sup>2</sup>	1.00	MW/m <sup>2</sup>
or				
	100	%	43	%
Black liquor flow	2200	tDS/24h	943	tDS/24h
	25.5	kgDS/s	10.9	kgDS/s
Net heat (from balance)	9200	kJ/kgDS	9200	kJ/kgDS
	234.3	MW	100.4	MW
Net heat per floor area (furnace heat loading)	2.34	MW/m <sup>2</sup>	1.00	MW/m <sup>2</sup>

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APPENDIX II Balance Curve Turpentine (Alfa pinene) LEL %LEL Tärpätintasapainoilmassa

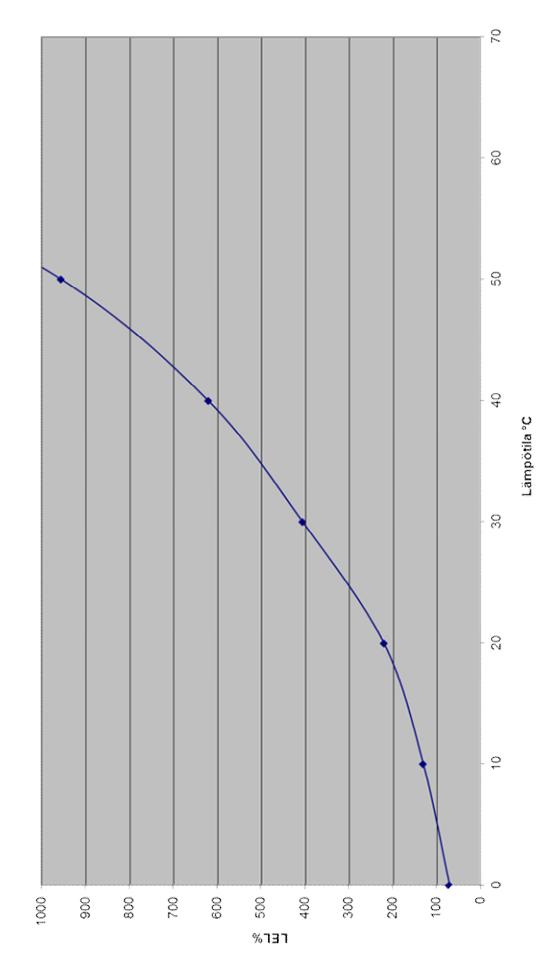


#### RECOMMENDED PROCEDURE FOR INCINERATION OF NON-CONDENSIBLE GASES APPENDIX II

131 %

APPENDIX III Balance Curve Methanol

#### RECOMMENDED PROCEDURE FOR INCINERATION OF NON-CONDENSIBLE GASES APPENDIX III



LEL %LEL metanoli