

LINDANE

Introductory information	
Name of the submitting Party/observer	CropLife International on behalf of Chemtura
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Chemical name (as used by the POPS Review Committee (POPRC))	Lindane (gamma isomer of hexachlorocyclohexane)
Date of submission	26 January 2006

(a) Sources, including as appropriate (provide summary information and relevant references)	
(i) Production data: Quantity Location Other	
(ii) Uses	Insecticidal seed treatments in the U.S.
(iii) Releases: Discharges Losses Emissions Other	Emissions from production of lindane by disposal of non-gamma isomers removed in the purification process have been noted to be of concern. Modern production technology processes these waste isomers into TCB and HCL thereby reducing or eliminating environmental contamination from these byproducts. Production process information is attached to this form.

(b) Hazard assessment for endpoints of concern, including consideration of toxicological interactions involving multiple chemicals (provide summary information and relevant references)	
<p>The <i>Evaluation</i> states that lindane has been identified as a B2 carcinogen, i.e., possibly carcinogenic to human by the International Agency for Research on Cancer. This conclusion, however, was reached in 1979 based upon studies of lindane contaminated with highly toxic isomers. A more recent evaluation of the carcinogenicity of lindane by Joint FAO/WHO Meeting on Pesticide Residues in 2002 concluded "In the absence for genotoxicity and on the basis of the weight of the evidence from the studies of carcinogenicity the Meeting concluded that lindane is not likely to pose a carcinogenic risk to humans." A similar conclusion was reached in the 2001 evaluation of the carcinogenicity data base by the US EPA. The toxicological endpoints described in the proposal are not relevant at the low levels of exposure associated with agricultural uses of lindane.</p>	

(c) Environmental fate (provide summary information and relevant references)	
Chemical/physical properties	
Persistence	<p>The <i>Evaluation</i> states that the half-life of lindane in soil is “reported to be two years.” In fact, however, the soil half-life of lindane is variable [c1]. In European soils the half-life was 40 to 70 days, and biodegradation is much faster in non-sterilized (bioactive) soil.</p> <p>[c1] IPCS International Programme on Chemical Safety. http://www.inchem.org/documents/hsg/hsg/hsg054.htm</p>
How are chemical/physical properties and persistence linked to environmental transport, transfer within and between environmental compartments, degradation and transformation to other chemicals?	<p>Technical hexachlorocyclohexane (HCH, mixed isomers) was used for many years as an insecticide in many parts of the world. Alpha-HCH is the primary isomer in tech. HCH, and also is the dominant isomer found in air, snow, and water in the arctic, with much lower levels of lindane, the gamma isomer of HCH.</p> <p>Data collected in 1994 at 39 locations from the Chukchi Sea across the North Pole to the Greenland Sea shows an average alpha-HCH/lindane ratio of >5 [c2]. Other studies, completed between 1986 and 1993 (cited in [c2]) showed similar alpha-HCH/lindane ratios. This ratio is similar to that in technical HCH, and suggests that the present HCH inventory in the arctic is the result of application of technical HCH rather than to contemporary application of lindane. Further, because isomerization of lindane to alpha-HCH is unlikely, decline of residues of alpha-HCH is due to abandonment of the use of technical HCH in most parts of the world [c3].</p> <p>These factors lead to the observed decline in levels of lindane and alpha-HCH in arctic regions.</p> <p>The remaining uses of lindane, in seed protectants, are not expected to contribute appreciably to levels in arctic areas. Earlier applications of HCH (mixed isomers) were largely foliar, allowing evaporation to the atmosphere and subsequent transport. Seed protectant uses bring lindane into contact with soil, to which it will adsorb and be a) metabolized and b) evaporate only slowly to the atmosphere.</p> <p>[c2] Jantunen & Bidleman. 1996. <i>J. Geophys Res.</i> 101:28837. Errata – ibid. 1997 102:19279. [c3] Walker, Vallero, & Lee. 1999. <i>Env. Sci. Tech.</i> 33:4373.</p>

<p>Bioconcentration or bioaccumulation factor, based on measured values (unless monitoring data are judged to meet this need).</p>	<p>A recent publication [c4] reports the continued finding of generally low and declining levels of residues of HCH (all isomers) in arctic fish, mammals, and birds. The levels are generally characterized as “not of concern” to the species or to humans consuming them. An estimate of the dietary intake of HCHs by humans in the arctic ranges between 3% and 20% of the Tolerable Daily Intake. As levels of HCHs in the arctic diminish, the dietary intake will also diminish.</p> <p>Further, the U.S. EPA has judged [c5] that although lindane bioconcentrates in organisms, it is also rapidly eliminated when exposure is discontinued. Therefore diminishing levels of lindane (and other HCH isomers) in arctic regions will lead to gradually diminishing levels in organisms.</p> <p>[c4] Indian and Northern Affairs Canada. 2003. Can. Arctic Cont. Assessment Report II.</p> <p>[c5] U.S.EPA. 2000. Lindane – Registration Eligibility Document, p. 41.</p>
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(d) Monitoring data (provide summary information and relevant references)

Detects of hexachlorocyclohexanes (HCH, all isomers) first occurred in the arctic in the 1970s and 1980s, when the use of mixed isomers was widespread [d1]. Diminished use of mixed isomers has led to recovery, i.e., lower environmental levels. Data from 1989 and 1990 showed net deposition of HCH isomers into the Arctic Ocean [d2], whereas more recent data show loss of HCH to the atmosphere [d3]. Hence the Arctic Ocean is undergoing cleaning, and HCH levels are decreasing in concert with diminished terrestrial uses.

Further, while lindane was one of the more common pollutants found in the arctic 10 years ago, its levels have dropped by more than 80% [d4]. This finding indicates strongly that past use of HCH and lindane, not current uses of lindane, is the source of HCHs in the arctic.

A recent report [d5] documents the decline in arctic levels of alpha-HCH during the 1980s and 1990s, and further notes a) equilibrium of the Arctic Ocean with respect to alpha-HCH and b) release of alpha-HCH back to the atmosphere. The latter is consistent with lower use rates of alpha-HCH. The same report shows a slight increase in levels of beta-HCH, from ocean currents rather than from atmospheric transport.

[d1] Li. 1999. *Sci. Total Env.* **232**:121.

[d2] Li *et al.* 1998. *Geophys. Res. Lett.* **25**:39.

[d3] Harner *et al.* 1999. *Env. Sci. Tech.* **33**:1157.

[d4] Hargrave. 1999. Reported in *Toronto Star* (March 5).

[d5] Arctic Monitoring and Assessment Program, 2002.

(e) Exposure in local areas (provide summary information and relevant references)	
<ul style="list-style-type: none"> - general - as a result of long-range environmental transport - information regarding bioavailability 	<p>Residues of HCHs in foodstuffs in China between 1978 and 1992 decreased by about 5x for rice, 127x for fish, and 32x for poultry, eggs, and meat [e1]. Further, alpha-HCH residues in pike muscle in Sweden declined along with usage of technical HCH (mixed isomers) [e2], as did levels of HCH isomers in arctic cod liver [e3]. Clearly, lower usage is associated with environmental recovery.</p> <p>[e1] Li <i>et al.</i> 1998. <i>Geophys. Res. Let.</i> 25:39. [e2] Breivik <i>et al.</i> 1999. <i>Sci. Total Env.</i> 239:151 [e3] Harner <i>et al.</i> 1999. <i>Env. Sci. Tech.</i> 33:1157.</p>

(f) National and international risk evaluations, assessments or profiles and labeling information and hazard classifications, as available (provide summary information and relevant references)
<p>US EPA Reregistration Eligibility Decision Document (http://www.epa.gov/oppsrrd1/reregistration/lindane/). The US EPA evaluated toxicology, residue, environmental fate and other relevant data in 2002 and concluded that seed treatment uses could continue.</p> <p>Joint FAO/WHO Meeting on Pesticide Residues 2002 (http://www.inchem.org/documents/jmpr/jmpmono/2002pr08.htm). The JMPR expert committee evaluated all relevant toxicological data at this meeting and concluded no additional studies were needed.</p> <p>ATSDR Toxicological (Profile http://www.atsdr.cdc.gov/toxprofiles/tp43.html). Comprehensive assessment of lindane and other hexachlorocyclohexane isomers by the US Centers for Disease Control.</p>

(g) Status of the chemical under international conventions
<p>Lindane is listed on Annex 2, Severely Restricted, of the ECE LRTAP POPs Protocol. The allowed uses greatly exceed the seed treatment uses, which are all that are being supported by Chemtura. www.unece.org/env/lrtap</p> <p>Both lindane and HCH(mixed isomers) are included in the PIC procedure under the Rotterdam Convention. www.pic.int</p> <p>Lindane is currently registered for seed treatment uses in the United States. (See (f) above).</p> <p>In 2002, PMRA Canada issued notices canceling lindane seed treatment products based upon occupational risks; after extensive hearings, a statutory Board of Review recommended that the Canadian Minister of Health direct PMRA to reconsider its cancellation decision. On January 17, 2006, PMRA on its own initiative advised Chemtura that it "intends to reconsider the occupational risk assessment..."</p>

LINDANE PRODUCTION PROCESS

The synthesis of lindane is made in two steps:

- Hexachlorocyclohexane (BHC) production
- Lindane extraction and purification

The first step is a chemical reaction which produces a mixture of different isomers of hexachlorocyclohexane. In the second one, the gamma isomer is extracted and purified. A third step must be considered for the waste treatment.

1.- BHC PRODUCTION

The enclosed Flow Sheet 1 shows the process.

The chlorine is piped in liquid state directly from a neighbouring plant located in the same chemical factory and it goes through a filtration and cooling unit, with brine at -15°C , to make sure that its temperature does never go up -5°C and that there are no gasifications. There is a panel of safety devices that cuts automatically the supply of chlorine in case something wrong is detected.

All equipment and pipes in this part are made of iron until they arrive to the chlorine injector in the reactors, where it is made of Teflon.

The liquid chlorine is directly injected into the reactors with a flow of 180 l/h. These reactors are made completely of standard glass materials and have: cooling body, lamp body and graphite circulator which formed a half closed circuit. In the circulator area the fresh benzene is injected at a rate of 1.600 l/h.

The solution is re-circulated, keeping the temperature around 45°C through water circulation at 20°C through the coolers. The half-life of the solution in the reactor is 3.2 hours.

The reactor has 36 lamps of 60 wat. of power each one, to provide the light used as catalyst.

Part of the reactor solution is purged towards a reaction ender ("finisseur") formed by a glass cylinder without cooling, in which there are 20 lamps identical to the reactor's.

There are four lines of reaction as the described one.

The reactors and the "finisseurs" have ventilations which lead the gases towards a condenser (refrigerated with brine), where the benzene is recovered and the incondensable gas is carried to a scrubber running in half closed unit. The purge

from the circuit is sent to the effluent treatment plant. All the recovering system and gas treatment equipment is made of glass.

The solution coming out of the “finisseurs” has a temperature of about 50 °C, a concentration of 24% w/w. (density 0,965-0,970 at 40 °C and 0,985 at 20 °C), a residual chlorine of 0.05 gr/l. and an acidity of 0.05 gr HCl/l.

Through a glass pipe the way outs of the four “finisseurs” are unified and sent to distillation system. This has four equipments working in series:

- First Tower, made in stainless steel AISI-316L + Ti, in it the distillation of about 40% of benzene is produced.
- Second Tower, also made of stainless steel AISI-316 + Ti, in it another 40% of benzene is distilled and a phase change is produced: from a BHC solution in benzene we get a benzene solution in BHC.
- First and Second Distillers made of steel lead lined, each of them eliminates 10% of benzene through a direct steam injection (azeotrope of lower boiling point).

The temperatures in each equipment are rising and benzene steams are recovered through glass or graphite condensers working with water at 20 °C.

The final product obtained is formed by melted BHC, which is carried to a flaker.

The obtained flakes can be used directly for the Lindane production as their content in benzene and water is less than 0,5%.

The condensed benzene is neutralized with aqueous solution of carbonate and hyposulphite, the aqueous phase is decanted and sent to the effluent treatment plan. The benzene is dehydrated through azeotropic distillation and it is sent to the benzene recycling tank, where the fresh benzene is added. From there the reactors are fed.

The facility works continuously, 24 hours a day, 7 days per week, producing an average of 30-32 Mt. of BHC daily.

The average composition of the BHC obtained is:

Alpha – HCH = 65 – 70 %
Beta – HCH = 7 – 9 %
Gamma – HCH = 14 – 15 %
Delta – HCH = 6 – 8 %
Other isomers = 3 – 5

2.- LINDANE EXTRACTION AND PURIFICATION

The process developed by Inquinosa for the production of Lindane is explained in the enclosed Flow Sheet 2.

Inquinosa has 3 lines of gamma extraction, that work in parallel, and one for recrystallization of Gamma-95 common for the three.

1.500 Kg. of crude BCH are loaded in the heat reactor along with 5.000 litres of methanol and then a selective extraction of the gamma isomer is done, controlling temperature, time and concentration conditions. By boiling the solution, the last traces of benzene are eliminated in form of an azeotrope.

The non-solved isomers (mainly alpha and beta) are separated through a centrifugal process in a basket centrifuge bottom discharge. The resultant cake is washed three times with methanol. The resultant waste 1 is a white solid of similar aspect than BHC (mainly alpha and beta isomers) and it is sent to a dryer, where the solvent is recuperated, and later to the cracking plant for the production of trichlorobenzene and hydrochloric acid.

The solution of the gamma isomer is sent to a crystallization process by cooling, in which temperature, time and concentration are also controlled.

The obtained crystals have a richness of gamma isomer of 95 – 97 % and are separated from the mother liquor by centrifugation, using a centrifuge similar to the previous one.

The mother liquor is piped again to the heat reactor, to make a new extraction of BHC. A part of the same (300 litres) is purged to avoid the saturation of unwanted products and is compensated with solvent that comes from the washing and the purification of Gamma-95, so the volume used for the extraction remains constant.

The purged solvent goes through a process of distillation in which second wastes are obtained containing mainly Delta-isomer, along with the other residues having a grease like aspect. They are sent also to the cracking-plant. The distilled solvent is purified by rectification and reintegrated to the productive process.

The solid named Gamma-95 is purified by recrystallization using the same solvent. For that, 500 Kg. are loaded in a heat reactor and later crystallized in a cool reactor. The formed crystals are separated from the mother liquors by centrifugation (it is used a centrifuge similar to the previous ones) and they are washed with solvent. They have a richness of gamma-isomer above of 99.5% so they constitute lindane. For lindane pharmaceutical quality, a second recrystallization takes place.

The lindane is dried in a rotational cylinder dryer and, depending on the wanted quality, can be packed for sale as crystal (for liquid formulations) or go through a milling process (micronised lindane for solid formulations and pharmacy) before being packed.

The mother liquor is recycled to the heat reactor for the recrystallization of a new batch of gamm-95. Part of the same (300 litres) is purged to a circuit of extraction of the BCH and compensated with washing solvent from the washing and solvent recuperated in the rectification or fresh solvent.

3.- WASTE TREATMENT

As it was explained, during the lindane production two kinds of wastes are generated:

- Waste 1, during the first step of gamma extraction.
- Waste 2, during the process for methanol purification.

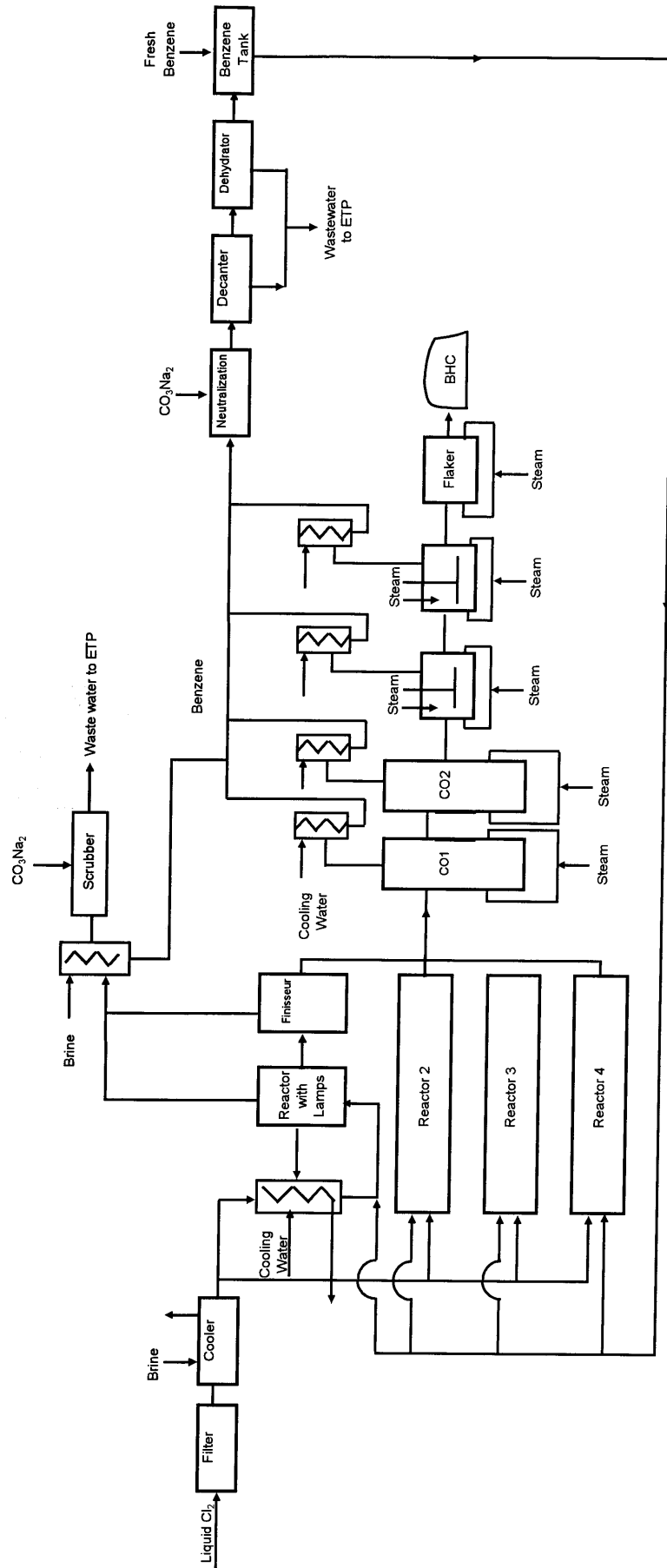
Both of them are sent to the cracking plant (integrated in the factory building) for producing trichlorobenzene and hydrochloric acid (see Flow Sheet 3). The starting point is different due to the physical state of the wastes:

- Waste 1 is a white solid and it can be dry at 75°C directly in a plough dryer for recovering methanol.
- Waste 2 is a yellow grease and it is dried in a different way. The product is smelted in a glass lined reactor at 100°C, using a nitrogen flow to eliminate the traces of methanol and solved in TCB then, in a second reactor.

The products obtained in the two drying lines are fed into the cracking stainless steel reactor. There are three reactors in the factory: two are working and one is in reserve. The cracking reaction is developed at 250°C using activated charcoal as a catalyst and it produces trichlorobenzene (TCB) and hydrochloric acid (HCl) in gas phase. The output is passed through an air cooler, where the TCB is condensed so from this point two streams are obtained:

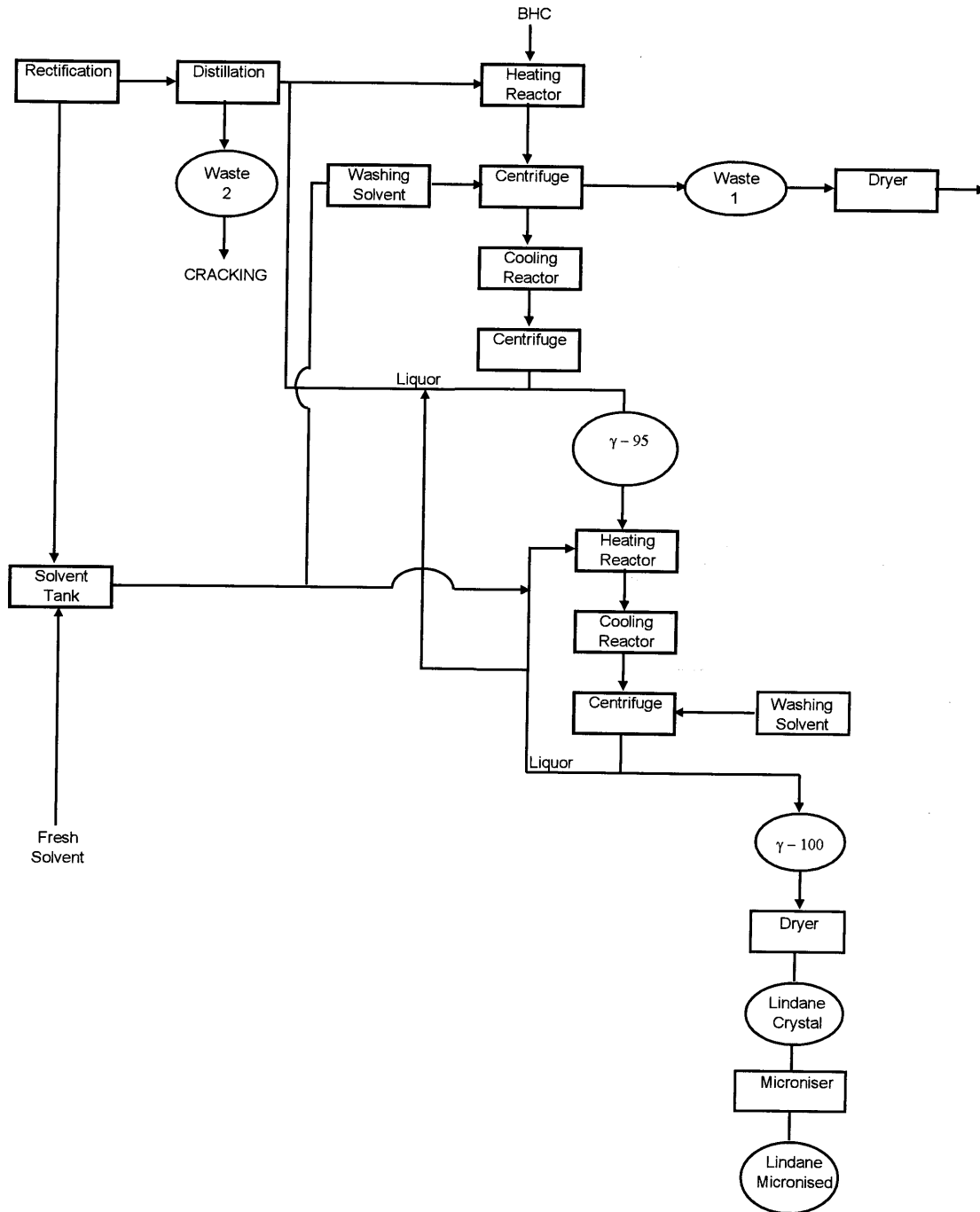
- The TCB fraction is sent to a glass decanter for eliminating the heavy fraction and then to two glass made stripping columns with air, where the hydrochloric acid traces are eliminated. The exit air is piped to the acid line and technical TCB can go to the storage tanks.
- The HCl fraction is sent to a glass made washing column where the TCB traces are eliminated using paraffin. The final step is the absorption of HCl gas into water in two glass made columns, producing a 33% concentrated solution which is piped to the storage tanks.

BHC PRODUCTION



LINDANE EXTRACTION AND PURIFICATION

FLWSHEET 2



**FLWSHEET 3
WASTE TREATMENT**