

**SFY94-XIV-48
DEVELOPMENT OF COMMERCIAL GRADE NAPHTHOLS
FROM DGC'S TAR OIL**

CONTRACTOR: Dakota Gasification Company

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PARTICIPANTS

<u>Sponsor</u>	<u>Cost Share</u>	<u>Revised Cost Share</u>
Dakota Gasification Company	\$795,000	\$265,000
ND Industrial Commission	<u>250,000</u>	<u>\$200,000</u>
Total	\$1,045,000	\$465,000

Project Schedule - 15 Months

Contract Date - 9/22/93
Start Date - 9/22/93
Completion Date - 3/31/95

Project Deliverables

Status Report - 1/30/94 ✓
Status Report - 5/30/94 ✓
Status Report - 8/15/94 ✓
Status Report - 10/31/94 ✓
~~Status Report - 12/15/94~~
Final Report - ~~3/31/95~~ 3/20/95 ✓

OBJECTIVE / STATEMENT OF WORK

The overall objective of this program is to develop the technology for the recovery of α and β naphthol from DGC's tar oil stream. A two-phase project is proposed. Phase I involves basic bench scale explorations to produce and identify commercially acceptable naphthols. In Phase II, pilot plant operations are proposed: 1) to demonstrate technology, 2) to obtain performance data for commercial plant design, 3) to produce trade sample quantities, and 4) to support an ongoing marketing effort. Markets exist for α and β naphthols, but not for mixed alkylated naphthols.

STATUS

The total amount of alpha-naphthol and beta-naphthol in DGC's tar oil stream is estimated at 1.3 million pounds per year, while the total amount of the homologous series of alkylated naphthols is nearly 8.7 million pounds per year. In addition, it is projected that nearly 1.5 million pounds per year of two indanol isomers are present, which might be recoverable (probably with some difficulty).

During the initial testing period of Phase I, a series of fractionations and extractions were done to isolate naphthol rich streams. The bottom 65.9 percent of the plant tar oil stream was first depitched and then fractionated. Distillate cuts were collected in the boiling range from C₉ phenols and indanols up through C₃ naphthols and separated into neutral and polar fractions by way of extraction with a multi-component solutizer solution. The polar fractions were analyzed by gas chromatography.

Batch distillations were performed to isolate C₉ and indanol fractions. A concentrated solution of sodium phenolate with an excess of free caustic was used to separate each distillate into neutral oil and polar substances. Technologies were also pursued to upgrade the naphthol and indanol fractions. Numerous alkylindanols were also found. Studies have been done to evaluate a method to convert the homologues to alpha-naphthol, beta-naphthol and phenol.

The results of Phase I testing showed a high concentration of alkylated naphthols. Phase II was designed to evaluate the Dynaphen Process developed by Hydrocarbon Research Incorporated (HRI). Dynaphen is a selective hydrotreating process.

Distillation and concentration pilot plants at DGC were operated to prepare quantities of naphthol-rich distillate. In the pilot plant the raw tar oil containing approximately 0.15 wt. % alpha-naphthol, 0.40 wt. % beta-naphthol, 0.91 wt. % C₁-naphthols, 0.45 wt. % C₂-naphthols, and 0.38 wt. % C₃-naphthols was upgraded to 0.55 wt. % alpha-naphthol, 1.50 wt. % beta-naphthol, 5.00 wt. % C₁-naphthols, 3.50 wt. % C₂-naphthols, and 1.95 wt. % C₃-naphthols. The distillation and concentration process involved multiple distillation and concentration steps. Atmospheric distillation of the raw tar oil was done to remove water and light naphtha. Vacuum distillation was used to remove heavy naphtha, phenol, cresylic acid, and neutral oil. In addition, vacuum distillation was used to produce naphthols-rich distillate and heavy pitch fractions. Proprietary processing steps were used to concentrate the naphthols while removing neutral oils. Samples of the raw and upgraded mixed-naphthol-rich tar oils were provided to HRI for evaluation.

The Phase II Dynaphen process tests conducted by HRI did not successfully convert the raw or upgraded mixed-naphthols into alpha- and beta- naphthols. The process did not appear to selectively convert the alkylated naphthols but instead appeared to dehydroxylate, that is produce benzene, toluene and naphthalene. Consequently, further research was terminated and the project ceased.