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THERMOCHEMICAL CONVERSION OF BLACK LIQUOR ORGANICS
INTO FUELS

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<p>A low-viscosity fuel oil has been prepared from black liquor by the following process: i) thermal treatment of black liquor at 300-350 °C under pressure (20 MPa) in the presence of excess alkali (NaOH), ii) removal of sodium from the black liquor primary oil by acid wash, and iii) catalytic upgrading of the sodium-free black liquor primary oil. The yield of primary oil was about 40 wt-% of the initial black liquor organics in the thermal treatment stage. The oil had a sodium content of 7 % (dry matter basis) and only about 1 % of the oil was distillable (< 260 °C). By washing the oil with dilute acid the sodium content dropped to 0.02 %. In this case the distillate yield was 11 %. After the catalytic (NiMo/CoMo) two-stage (30 min at 280 °C and 60 min at 390 °C) hydrotreatment an oil yield of 88 % was obtained and the distillate yield was 51 %. The total loss of organics in the wash and upgrading stages was 20-25 %.</p>	

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<p>Mustalipeästä on onnistuttu valmistamaan polttonestettä seuraavalla prosessilla: i) mustalipeän paineellinen (20 MPa) lämpökäsittely alkalilisäyksellä (NaOH) lämpötila-alueella 300 - 350 °C, ii) natriumin poisto öljystä happopesulla, ja iii) natriumvapaan öljyn katalyyttinen jatkojalostus. Mustalipeän hydrausöljyn saanto oli noin 40 paino-% mustalipeän orgaanisesta aineksesta ja öljyn natriumpitoisuus 7 % kuiva-aineesta. Vain noin 1 % öljystä oli tislautuvaa (< 260 °C). Happopesussa öljyn natriumpitoisuus aleni 0,02 %:iin. Tislesaanto oli tällöin 11 %. Katalyyttisellä (NiMo / CoMo) kaksivaiheksittelyllä (30 min 280 °C:ssa ja 60 min 390 °C:ssa) saavutettiin 88 %:n öljysaanto ja 51 %:n tislesaanto. Orgaanisen aineksen kokonaishäviö pesu- ja jalostusvaiheissa oli 20-25 %.</p>	

FOREWORDS

The publications for this licenciate's thesis have been written during the "black liquor liquefaction" project, which was initiated in 1984 in the Laboratory of Fuel and Process Technology of the Technical Research Centre of Finland (VTT). The project is funded by the Finnish Ministry for Trade and Industry (KTM) and is presently a part of Finland's national energy research programme JALO (Fuel conversion). The project members are: PhD Paterson McKeough (project leader), TechD Raimo Alén (senior research scientist), Prof. Allan Johansson (research professor) and Ms. Anja Oasmaa, M.Sc. (research scientist).

I wish to express my sincere gratitude to Raimo Alén, the supervisor of my work at the Laboratory of Wood Chemistry, Helsinki University of Technology, for his valuable guidance and encouragement during this work. Special thanks are due to PhD Paterson McKeough for his useful ideas concerning the upgrading procedure. Thanks are due to technicians, Mr. Reijo Häkkinen for carrying out the experimental runs, and Ms. Outi Kovanen, Ms. Mirva Mattila and Ms. Katja Heiskanen for their careful work on product work-up and analyses. Thanks are also expressed to the personnel of the analytical section of the Laboratory.

I also wish to express my deep gratitude to prof. David G. B. Boocock and his working group at the University of Toronto for an extraordinary encouraging working atmosphere during my stay in the group.

Espoo, October 1991

A handwritten signature in cursive script, appearing to read 'Anja Oasmaa', written in dark ink on a white background.

Anja Oasmaa

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PUBLICATIONS

This licentiate's thesis summarises and discusses the following publications:

- I Alén, R., McKeough, P., Oasmaa, A. & Johansson, A. Thermochemical conversion of black liquor in the liquid phase. *J. Wood Chem. Technol.* 9(1989), p. 265-276.
- II McKeough, P., Alén, R., Oasmaa, A. & Johansson, A. Thermochemical conversion of black liquor organics into an oil product. I. Formation of the major product fractions. *Holzforschung* 44(1991), p. 445-448.
- III Alén, R. & Oasmaa, A. Conversion of glucoisosaccharinic acid by heating under pressure. *Acta Chem. Scand. B* 42(1988), p. 563-566.
- IV Alén, R. & Oasmaa, A. Thermochemical conversion of hydroxy carboxylic acids in the liquid phase. *Holzforschung* 43(1989), p. 155-158.
- V Oasmaa, A. & Boocock, D. G. B. The catalytic hydrotreatment of peat pyrolysate oils. *Can. J. Chem. Eng.* (in press).
- VI Elliott, D. C. & Oasmaa, A. Catalytic hydrotreating of black liquor oils. *Energy & Fuels* 5(1991)1, p. 102-109.

These papers are referred to in the following text by the Roman numerals I-VI.

1 Background

About 7 % of the total Finnish energy demand is achieved by burning the waste liquor ("black liquor") originating from the kraft pulping industry /1/. Presently black liquor is burned in a Tomlinson-type recovery boiler. However, this furnace has several drawbacks /2-4/: the low thermal efficiency of the energy recovery, the limited capability for electricity generation, the high capital costs of the recovery equipment, and operational hazards.

In 1984 the Laboratory of Fuel and Process Technology at the Technical Research Centre of Finland (VTT) initiated a major research project on black liquor thermal treatment. The primary objective of the project, to which also this study belongs, was to develop a process which could replace the recovery boiler of the pulp mill. This process can also be applied in parallel to the recovery boiler. If the boiler is the bottleneck of the mill, this latter application can lead to an increase in pulp production. Up to 20 % of the total black liquor stream can be diverted without disturbing the chemical reactions in the recovery furnace /5/.

Two types of thermal treatment are being studied at our laboratory, gasification and liquefaction of black liquor. The objective of the gasification research is to get a clean, combustible gas for electricity generation in a combined-cycle process /6,7/. The process development on liquefaction is being discussed in this paper. The present process version is presented in the Fig. 1.

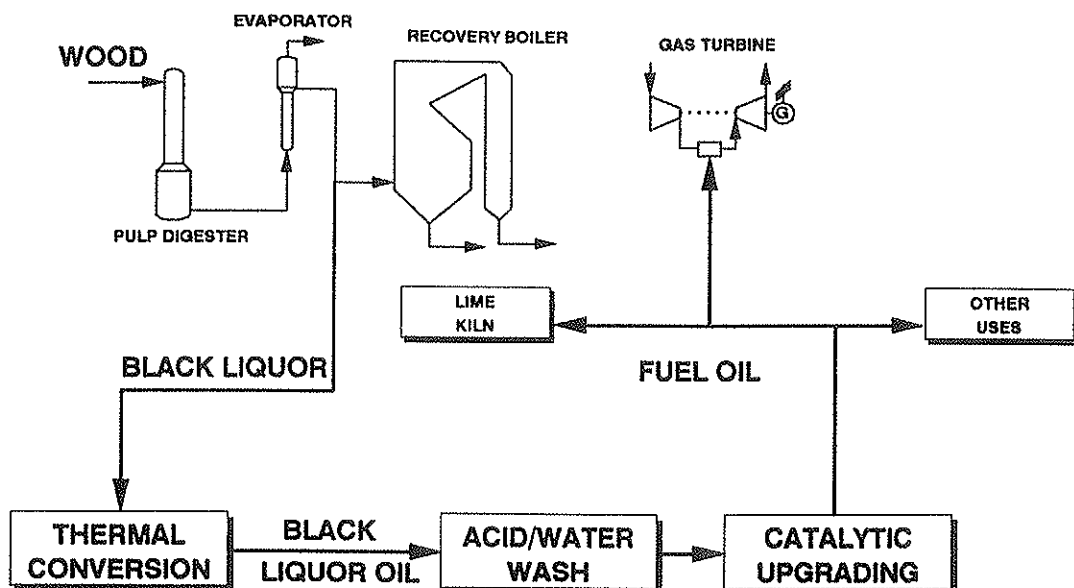


Fig. 1. Upgrading of black liquor into fuel oil.

During delignification about half of the organic material of the wood is dissolved into the cooking liquor. Kraft black liquor has been thoroughly analyzed /8-11, III,IV/. It consists mainly of degraded lignin, aliphatic carboxylic acids (carbohydrate degradation products), and inorganics (mainly sodium). A major amount of the sodium is bound to the organic part of the black liquor, e.g. to lignin and aliphatic acids. The composition of the black liquor depends greatly on the raw material and cooking conditions. Typical compositions of black liquor are presented in the Table 1 /9/.

Table 1. Typical composition of the dry matter (%) of pine and birch kraft black liquor /9/

Component	Pine	Birch
Aliphatic carboxylic acids	31	32
Formic	6	4
Acetic	4	9
Glycolic	2	2
Lactic	3	2
2-Hydroxybutanoic	1	5
3,4-Dideoxypentonic	2	1
3-Deoxypentonic	1	1
Xyloisosaccharinic	1	2
Glucoisosaccharinic	7	3
Others	4	3
Lignin	33	27
Extractives	5	4
Other organics	3	8
Inorganics*	28	29

* Including sodium bound to organic material; the amount of this sodium in both cases is about 12 % of the total dry matter.

The preliminary experiments /2-4,12/ indicated that when black liquor is heated (300-350 °C) under pressure (20 MPa) in a reducing (H₂, CO) atmosphere, a hydrophobic oil-phase separates from the black liquor. El-Saied and Oelert /23/ noticed the same phenomena earlier when they treated sulphite spent liquors under similar conditions. The formation mechanism and origin of the oil-phase were largely unknown. Hence, the first part of this research aimed to i) clarify the formation of the oil-phase /III,IV,8,13/ and ii) optimize the yield and quality of the oil /I/.

These studies resulted in another process version, where a certain amount of alkali is added to the black liquor before thermal processing /II/. In this process concept a reducing gas phase was no longer necessary. The role of alkali in high-pressure treatment of black liquor was first noticed by Hägglund and co-workers /14/, who reported that the yields of tar, methanol, and gases depend on the amount of alkali (e.g. NaOH) added. In the work by Enkvist /15,16,17/ a similar alkali addition to black liquor before the thermal treatment was used to facilitate the production of certain organic chemicals such as phenols.

The black liquor primary oil obtained with this method is a high-molecular-weight oil with a high content of sodium (7 % of the dry matter). The oil is not suitable for fuel use as such. The objective of the third part of this work, upgrading, was to remove the inorganics and to improve the quality of the oil for use as a fuel oil in a lime kiln or in a gas turbine. The research focused on finding the most promising method for upgrading the oil into useful fuels /VI/. A preliminary experimental study on the catalytic upgrading of biomass oils /V/ proved useful for obtaining basic experience in this area.

The catalytic upgrading of woody biomass has been widely studied. Typical reaction temperatures and pressures for hydrotreating are 250°C to 450°C and 7.0 to 20.0 MPa /30,33/. Elliott et al. /21,27,28,29,32/ have developed a two-step hydrotreating process for thermally unstable pyrolysis oils from wood. During the first stage at 250-280°C the reactive groups in the oil stabilize and do not form coke at the hydrotreating temperatures.

Elliott et al. /24-29,31/ also concluded that the most suitable catalysts for hydrotreating phenolics are palladium, copper chromite, cobalt and nickel, with nickel and cobalt being the most active ones. Churin /34,44/ reported that, if the oil contains nitrogen and sulphur, the only supported-type catalysts able to work under this severe conditions are cobalt-molybdenum and nickel-molybdenum supported on alumina or silica alumina. The sulphide form of these catalysts is much more active than the oxide form /24-27,30,34/ and, in the case of the cobalt-molybdenum, much of the specificity for hydrodeoxygenation is retained. In cases requiring a stronger hydrocracking activity, more acidic supports like silica-alumina, zeolites and alumino-phosphates have shown promise in place of the alumina as a support for the CoMo and the NiMo catalysts /30,43/. The sodium can poison the catalyst and therefore it is recommended that it should be removed before the hydrotreating /27,35,37,38/.

Upgrading with zeolites is an evolving technology /44-48/ to produce selectively high quality hydrocarbon fuels, like gasoline and diesel, or aromatic chemicals from biomass oils. No reducing gas is required and the reaction is carried out at atmospheric pressure. The typical temperatures are 350-450°C. The feed oil has to be

volatile. However, these catalysts are not yet generally available.

Churin *et al.* /33,34,44/ have emphasized that the nature of the oils to be treated is very important and suggested that bio-oils derived from lignin constitute the best feed for hydrotreatment. Ratcliff *et al.* /43/ have developed catalysts for hydrotreating lignin and model compounds. Their aim is to produce phenols. Piskorz *et al.* /42/ have catalytically hydrotreated lignin-derived pyrolysis oils. Yields of 61 to 64 % were obtained. Meier *et al.* /39,40/ have liquefied wood and lignocellulosic materials. A high yield of liquid hydrocarbons was obtained by using palladium (1 %) on active charcoal. Palladium was more active than NiMo. The catalysts were not sulphided. At optimum conditions a 68 % oil yield was obtained from kraft lignin. Meier /39,40/ reported that the oil yield increases with increasing pressure. The initial hydrogen pressure should be at least 10 MPa.

2 Process development for thermal treatment of black liquor organics

Several combinations of gas phases (H_2 , CO, CO_2 , N_2), temperatures (300 °C, 350 °C), pressures (initial pressures 0 - 7 MPa), and additives (NaOH, CaO, Na_2CO_3 , Na_2S , wood oil distillate, cellulose) were studied in order to optimize the yield and quality of the black liquor oil product /1,2-4,12/. The schematic representation of the process concept, including recovery of cooking chemicals, is shown in Fig. 2 /9/.

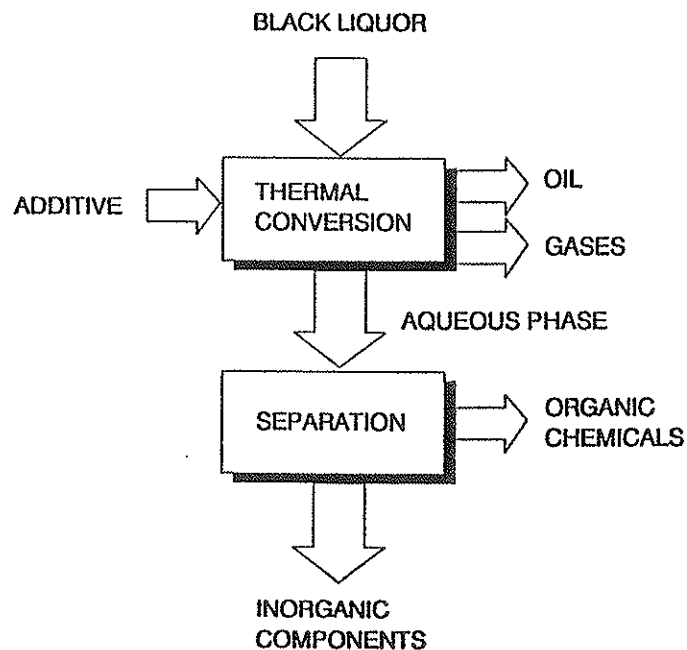


Fig. 2. Schematic representation of the thermal treatment process /9/.

The black liquor primary oil was too heavy to be analyzed by conventional methods, like gas liquid chromatography (GLC). Hence, the most important quality criteria used for the oil were relative molecular weight distribution and solubility in organic solvents such as tetrahydrofuran (THF). The yields of different product groups for the basic process types are presented in the Table 2 /I,12/.

Table 2. Conversion of black liquor organics into main product groups (% of the initial total organics) /I,12/^a

Product	300 °C			350 °C		
	CO	H ₂	N ₂	CO	H ₂	N ₂
Organic phase	41	50	64	40	42	44
Aqueous organics	70 ^b	32	24	20 ^b	21	14
Other, mainly CO ₂ ^c and H ₂ O	29	18	12	55	37	42
THF-solubles in organic phase, % of the oil dry matter	31	6	10	24	29	14

^a Reactions for 45 minutes at about 20 MPa pressure.

^b Including the portion formed from carbon monoxide.

^c In part chemically bound in sodium carbonate/bicarbonate.

The most promising process version so far is the so-called alkali-addition process. In this concept black liquor is treated for 45 minutes at 350 °C under nitrogen after a sodium hydroxide charge of 20-45 % of the mass of black liquor dry solids. When using high loads of alkali (over 40 % of black liquor dry solids), the oil phase is dissolved and recovered only by acidification. The oil yields (Table 3) were in the same range as those obtained without alkali addition (Table 2), but an obvious improvement in the quality of the oil was noticed (Fig. 3). It was concluded that the alkaline medium promotes favourable reactions of the lignin oil-precursors /II/.

Table 3. Effect of process conditions on the quantity and quality of the organic-phase product and on the pH after treatment /II/ ^a

	Amount of alkali (NaOH) added, % of black liquor dry solids			Without alkali addition ^b	
	19.0	27.8	43.7	Without reducing gas	Reducing gas (H ₂)
Yield of organic oil-like product, % of initial organics	44	42	38	44	42
Description of organic-phase product	High viscosity oil	Medium viscosity oil ^c	After acidification, low viscosity oil	Solid product	High viscosity inhomogeneous oil
pH after treatment ^d	10.4	10.8	13.9	9.0	9.0

^a Reactions for about 45 minutes at 350 °C.

^b From Ref. 12.

^c Viscosity 115 cSt at 80 °C.

^d Initial pH was 14.2.

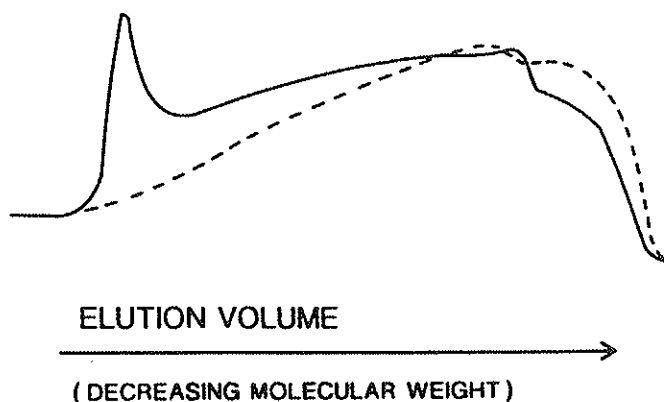


Fig. 3. Comparative gel permeation chromatograms for the THF-soluble fractions of two organic-phase products /II/.
Product A (—): formed under H₂ without alkali addition (350 °C / 45 min); 59 % of product THF-soluble.
Product B (---): formed under N₂ with NaOH addition of 27.8 % of black liquor dry solids (350 °C / 45 min); 66 % of product THF-soluble.

3 Aqueous phase studies

This part of the research was aimed to clarify especially the role of aliphatic carboxylic acids (hydroxy acids and formic and acetic acids) in the formation of the oil-phase. The hydroxy acid fraction was separated from the black liquor /18/ and the reactions were studied under conditions corresponding to those of the black liquor conversion process. The same treatment was also applied to α -gluco-isosaccharinic acid, the main carboxylic acid component in pine kraft black liquors /III,IV/.

The degradation of the hydroxy acids into lower carboxylic acids took place (Fig. 4). The main conclusion from these studies was that thermal degradation of the aliphatic acid fraction in black liquor is influenced only by temperature and reaction time, and that it is not significant source of oil-like products (the oil yield was 2-5 %) /III,IV/. Later work by Alén /13/ and Alén & McKeough /11/ showed that the lignin fraction of the black liquor is more amenable to reduction by a reducing atmosphere than the aliphatic acid fraction.

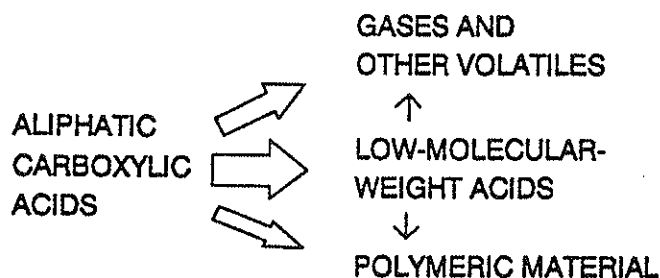


Fig. 4. The possible reaction routes of the hydroxy acid fraction of black liquor at high temperature (300-350 °C) and pressure (15 MPa) under reducing atmosphere (CO, H₂).

4 Washing of primary oils

The oil from the alkali-addition process contained a considerable amount of sodium (7 % dry basis), which affects its volatility and is a problem in its further processing. The major part of the sodium is present in organic salts dissolved in an entrained aqueous phase within the oil, although some of it was also bound chemically to the oil material.

By using a dilute acid wash the sodium content of the oil was reduced to 0.02 % with a simultaneous 16 % loss of organics. The consumption of the acid was 0.4 g/g dry oil. One of the main aims of the ongoing research is to minimize the consumption of acid in the washing step. The use of pure water was prevented by the fact that the oil is partly water-soluble /19,20/.

5 Preliminary attempts at upgrading biomass oils

A co-operative project between the University of Toronto and VTT was carried out for obtaining the required experience concerning upgrading of biomass oils. In this project peat pyrolysis oil was upgraded catalytically (sulphided CoMo on alumina) at high temperatures (390 °C for two hours) and under hydrogen pressure (21.5 MPa) /V/. Analysis by HPLC, FTIR and C¹³-NMR showed that the structure of the biomass oil had been partly cracked and hydrotreated during the processing. One of the major objectives of the catalytic treatment was the removal of the heteroatoms, oxygen, nitrogen and sulphur, of which the first predominates. The oxygen content of the oil was lowered from 22 % to 3 % in the process.

The experiences gained from this study, especially concerning the catalyst and its sulphiding method, feed/catalyst-ratio, and product work-up procedure, were used when upgrading the black liquor primary oil at VTT /V,VI/.

6 Catalytic upgrading of black liquor primary oils

The feed for upgrading was i) black liquor primary oil, or ii) acid-washed (sodium-free) oil. The primary oil was produced by treating the black liquor (27.8 wt% solids) at 350 °C for 30 minutes after a sodium hydroxide charge of 27.7 wt% (of black liquor dry solids). In some experiments also water was added to the black liquor oil in order to transfer the sodium from the oil into the water phase during the processing. Commercial CoMo and NiMo catalysts in their sulphided forms and on different supports (Al₂O₃, zeolite) were tested /VI/.

When using a temperature level of 385-405 °C an oil product of low-quality was recovered. However, Baker and Elliott /21/ have noticed that some wood-oils need a special stabilization step at lower temperatures. For this reason, in these experiments a temperature profile of 280 °C for 35 min / 380 °C for 40-245 min was used /VI,22/.

The oil yields ranged from 64 to 87 %. The highest oil yields, 84-87 %, were obtained in catalytic experiments using black liquor feed oil as raw material. The corresponding yield of distillate (< 260 °C) was 9 %. An acid wash of the oil was carried out (the sodium content of the dry oil was 10.6 %) and the yield of distillate increased to 23 %. Lowest yields were recovered at high temperature (405 °C) (the formation of gas), and in the experiments where water was added to black liquor primary oil before processing (some organics are water-soluble). The best quality oil product, 42 % distillate yield, was obtained by using the acid-washed (sodium-free) oil. The oil yields were, in this case, 75-79 %. Also a high-quality oil product, 32 % distillate yield, was recovered in water-addition runs (oil yields from 67 to

73 %). The main quality criteria for the oil were the distillability of the oil, the molecular weight distribution (HPLC/GPC), and the solubility in THF /VI/.

It was found that the sodium present in the oil had a negative effect on catalytic activity and retarded the hydrotreating reactions. Hence, it was evident that the sodium should be removed either before the hydrotreating (acid wash) or at the same time by adding water (a major part of the sodium compounds will dissolve in water during processing) /VI/.

In a recent study /22/, a higher yield of distillate, (51 %), has been obtained using acid-washed black liquor oil and two stage hydrotreating with a higher reaction temperature (390 °C) than in earlier runs. Duplicate experiments are necessary to confirm the influence of temperature on improving the quality of the oil. Longer residence time (245 min) increases only slightly the distillable portion of the oil. No clear difference in the activities of the catalysts was noticed. The upgrading data for some experiments is presented in Table 4 /VI,22/. Fig. 5 presents an overview of the best upgrading results achieved so far /22/.

Table 4. Upgrading data /VI,22/

Run no.	3 (89)	19(89)	8 (89)	9 (89)	10(89)	12(89)	6 (91)	9 (91)
Raw material	BLFO ^a	BLFO	BLFO	ACID-WASHED BLFO	BLFO	ACID-WASHED BLFO	ACID-WASHED BLFO	ACID-WASHED BLFO
Extra water	no	no	no	no	yes	no	no	no
Catalyst ^b	CoMo	no	CoMo	CoMo	CoMo	NiMoI	NiMoII	NiMoII
H ₂ , bar	70	70	70	70	30	70	70	70
Ts, °C	no	280 °C	280 °C	280 °C	280 °C	280 °C	275 °C	280 °C
Residence time, min	-	40	35	35	40	40	50	50
Tr, °C	405 °C	380 °C	380 °C	380 °C	380 °C	380 °C	380 °C	390 °C
Residence time, min	130	70	65	65	65	75	35	80
Yields (dry), wt% maf feedstock								
oil	64	74	85	75	67	79	84	88
distillate	14	22 ^c	23 ^c	27	32	42	40	51

^a BLFO = black liquor feed oil.

^b CoMo = cobalt-molybdenum on alumina. NiMo I = nickel-molybdenum on alumina. NiMo II = nickel-molybdenum on zeolite.

^c After acid-wash of the product oil.

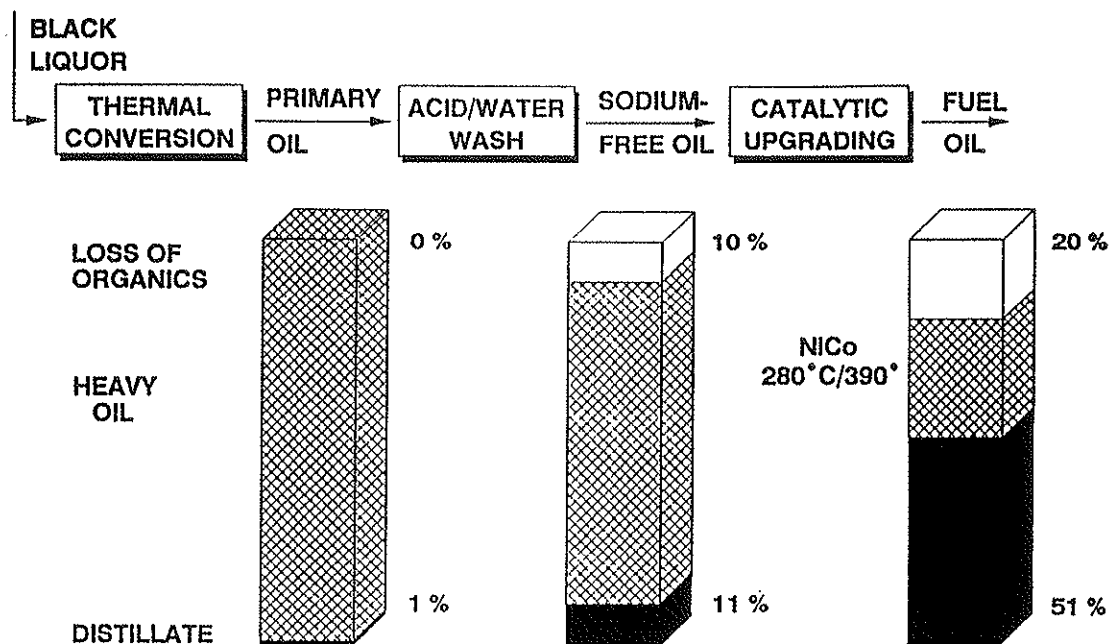


Fig. 5. Upgrading of black liquor oil. Product yields and quality /22/.

The light fraction (20 % of the dry distillate) of the upgraded product oil consists mainly of cyclic hydrocarbons and one- or two-ring aromatics. The heavier fraction (35 % of the dry distillate) contains mainly two- and three-ring aromatics with oxygen functionality. The heavy residue (boiling point over 500 °C) is most likely highly complex aromatics with relatively high oxygen content /22/.

7 Conclusions

The most relevant conclusions of this work can be briefly summarized as follows:

- By treating black liquor at high temperature (300-350 °C) with alkali or under a reducing atmosphere (H₂, CO) at high pressure (20 MPa) a hydrophobic oil phase (organic oil yield about 40 % of black liquor organics) is formed.
- The primary oil is derived mainly from the lignin constituents of the black liquor while the other main organic component of black liquor, the aliphatic carboxylic acid fraction, is mainly decomposed into low-molecular-weight acids and volatile compounds.
- The quality of the product formed using alkali addition is higher than that formed under reducing atmospheres.
- The best-quality primary oil is obtained by heating the black liquor after a sodium hydroxide charge of 30-45 % (of the weight of black liquor dry solids) for 45 minutes at 350 °C under an inert atmosphere.
- By washing the black liquor primary oil with dilute acid, the sodium content of the oil (7 %) was lowered to 0.02 %.
- A useful fuel oil (oil yield 88 %, distillate yield 51 %) was obtained by hydrotreating the acid-washed oil in the presence of sulfided catalyst (NiMo, CoMo) using two-stage temperature treatment (280 °C / 390 °C) under hydrogen pressure (20 MPa).
- The total loss of organics during the wash and upgrading stages was 20-25 %.

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