Efficient utilization of waste tall oil from the kraft pulp industry

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Tall oil, a by-product of the pulp industry, is a potential source of aromatic and olefinic hydrocarbon fuels.

Tall oil was discovered in the late 1800s as a natural product of pine wood. It represents the ether extractable nonlignin noncellulosic portion of the wood. Tall oil content of the pine species is about 3 wt% of the dry wood. In practice, tall oil is produced as a by-product in the kraft pulping industry. During the pulping operation, fatty and rosin acids present in the wood are saponified by the pulping liquor. The tall oil soap is washed from the pulp and is carried with the black liquor to the evaporators. It can then be skimmed from partially evaporated black liquor with typically 25-35 wt% dissolved solids. In a crude tall oil (CTO) plant, these soap skimmings are reacted with sulfuric acid. The aqueous phase containing precipitated lignin and spent sulfuric acid is later neutralized and returned to the mill recovery system. Typically, two metric tons of soap will yield one metric ton of CTO; i.e., for every metric ton of pulp produced, 30-40 kg of crude tall oil is produced (*1*). The quality of the oil varies widely, depending on such factors as geographic location, climatic conditions, types of wood, and production techniques. Since tall oil value is very small relative to the pulp produced, little care is exercised to collect all the tall oil available or to implement changes requiring capital investment to produce a higher quality product.

A typical composition of crude tall oil is presented in **Table I.** The two major chemical structures represented are rosin acids and fatty acids, in addition to nearly 35 wt% of neutral or unsaponifiable material (*1*). The rosin acids are diterpene carboxylic acids based on an alkyl substituted perhydrophenantharene ring structure. The fatty acids are predominantly 18-carbon, straight-chain mono- or di-unsaturated fatty acids. The approximate analysis of each fraction is also given in Table I. Among the rosin acids, abietic, neoabietic, and palustic acids predominate while oleic and linoleic acids are the main components of the fatty acids group. Unsaponifiables basically consist of hydrocarbons and long chain alcohols. These rosin and fatty acids contain 10-12 wt% of oxygen in their molecules.

Currently all of the crude tall oil is refined by fractional vacuum distillation in the presence of steam to produce fatty acids, rosin acids, distilled tall oil, tall oil heads, and tall oil pitch (*1*). For instance, Bergvik Kemi, a subsidiary of the Stora Kopparberg group in Sweden, has a fractionating plant with a capacity of 120,000 metric tons/year representing 80 wt% of Swedish crude tall oil capacity. Steam is used to lower the boiling point of the tall oil and to prevent anhydride formation and decomposition at the high refining temperatures. The fractionating towers generally operate at 200-285°C and 13.3 kPa. The major current concern is the cost of the energy required for distillation. The tall oil rosin and fatty acids find applications in the manufacture of dimer acids, alkyd resins, paints, adhesives, printing inks, detergents, and emulsifying agents. Tall oil heads contain lower boiling fatty acids and are used for the production of palmitic acid. Distilled tall oil has many uses where its liquid nature and mixed rosin and fatty acid content result in favorable product characteristics. Tall oil pitch is mainly used in rubber and plastic goods.

Due to its odor and complex nature, the direct substi-

I. Composition of crude tall oil, wt %

Abietic acid	23	
Palustic acid	9	
Neoabietic acid	24	
Dihydroxyabietic acid	4	
Isoextropimaric acid	4	
Unknown	36	
	100	
Total rosin acids, %		35
Oleic acid	47	
Linoleic acid	44	
Linolenic acid	2	
Saturated acids	7	
	100	
Total fatty acids, %		30
Phytosterols	32	
Alcohols	14	
Hydrocarbons	54	
	100	
Total unsaponifiables, % (Distilled tall oil, tall oil heads and tall oil pitch)		35

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II. Overall product distribution for tall oil-tetralin experiments

Run no.	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*
Temperature, °C	370	380	390	405	370	380	390	405
Space velocity, h^{-1}	2.5	2.5	2.5	2.5	3.6	3.6	3.6	3.6
Run time, min	60	65	60	60	60	60	60	38
			Product distribution, wt%					
Organic distil.	57.2	54.0	48.1	49.8	55.2	57.7	58.4	54.4
Residual oil	2.9	4.3	5.9	7.2	14.0	5.5	5.3	4.5
Water	15.9	16.2	15.8	15.1	16.4	16.7	15.3	13.7
Gas	18.4	19.3	22.5	23.2	10.8	17.6	18.9	23.8
Coke	4.4	3.7	2.7	1.9	2.3	2.4	1.7	2.9
Unaccounted	1.2	2.5	5.0	2.8	1.3	0.1	0.4	0.7
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

tution of tall oil for existing products is ruled out. It can be burned for energy (*2, 3*) and its derivatives have also been cited as useful additives to inhibit corrosion in diesel fuel, kerosene, and gasoline. Wernersson (*4*) found that a mixture of crude tall oil (up to 60 wt%) and heavy fuel oil may be used to operate a lime kiln in a kraft mill.

Secor and Lewko (*5*) tested crude tall oil blended with diesel as fuel for a diesel engine. In their studies, they also tested a de-pitched tall oil where over 50 wt% of the pitch in the crude tall oil was removed using a thin film evaporator at elevated temperatures and reduced pressures. Their results indicated that the specific fuel consumption was 5–15% higher for the blends. There was no evidence of engine wear or deposits, although a severe increase in combustion chamber deposits and fuel pump wear was observed. The use of crude or de-pitched tall oil in a diesel engine was, therefore, not recommended.

Alternative applications of crude tall oil, such as its catalytic conversion to more useful products, have not been explored. Nearly two decades ago, Mobil discovered a high silica zeolite, HZSM-5 (*6*), which has since found applications in a number of commercially important reactions. These include the conversion of methanol (*7*) and ethanol (*8*) to gasoline range hydrocarbons, isomerization of xylenes (*9*) and hydrodewaxing of oils (*10*). Later, Weisz *et al.* (*11*) and Haag *et al.* (*12*) explored the possibility of using HZSM-5 to convert vegetable oils such as castor, corn, jojoba, and other plant extracts to liquid and gaseous fuels over HZSM-5. Similar studies were carried out for palm oil (*13*), coconut and walnut oils (*14*), canola oil (*15, 16*), and depitched tall oil (*17*). Prasad *et al.* (*15, 16*) found that by using HZSM-5, 60–95 wt% of canola oil was converted to hydrocarbons, light gases, and water with the liquid product containing 60–70 wt% of aromatic hydrocarbons.

All these studies indicate that a variety of oxygenates can be converted selectively to hydrocarbon products by utilizing the strong acid properties and the intracrystalline network (*18*) of HZSM-5 which make it a highly active and shape selective catalyst. Its pore sizes are intermediate between small-pore and large-pore zeolites which, at room temperature, exclude the entry of highly branched molecules with over 9 or 10 carbon atoms. However, unlike small pore zeolites, these pores permit the entry of simple aromatic and branched molecules necessary for their cracking. The Saskatchewan Research Council has also shown the feasibility of a process for converting oils such as canola into diesel fuel products by using conventional refining technology (*19*).

Despite being considerably cheaper relative to the above vegetable oils, crude tall oil upgrading over HZSM-5 has not been studied. The objective of this investigation was to explore the possibility of converting the crude tall oil to hydrocarbons in the same way as for the vegetable oils. Due to a high viscosity and a large content of high boiling pitch in CTO, its flow characteristics are poor, which lead to many operational problems during upgrading. Similar problems encountered in the coal liquefaction industry also have been handled in the past 25 years by using some organic solvents such as tetralin with the feed. In this work, tetralin and steam were used as diluents.

Experimental section

The catalyst, HZSM-5, was prepared according to the procedure described in U.S. Patent 4,112,056 (*20*).

The catalytic conversion was carried out at atmospheric pressure in a continuous, downflow fixed bed microreactor. The reactor was a 9-mm ID, 510-mm long stainless steel tube placed coaxially in a furnace. About 1 g of the catalyst (500–1410 μm particle size) was held in the middle of the tube. Crude tall oil was fed to the reactor by a syringe pump at a weight hourly space velocity (WHSV) of 2.5–5.8 h^{-1}. When tetralin was used as a co-feed, it was mixed with the crude tall oil, and the mixture was fed to the reactor. However, in experiments with steam, a separate pump was used to feed water through a tee joint located just above the reactor tube. The products were collected over the entire run period, about 1 h. The products were cooled by an ice-salt mixture and were separated into gas and liquid fractions. The liquid product was condensed in a trap, whereas the gaseous product was collected over a saturated brine solution. The aqueous layer of the liquid product was separated, and the organic product was

III. Overall product distribution for tall oil-tetralin experiments in the presence of steam

Run no.	*9*	*10*	*11*	*12*	*13*	*14*	*15*	*16*	*17*
Temperature, °C	370	380	390	405	370	380	390	405	380
Space velocity, h^{-1}	2.5	2.5	2.5	2.5	3.6	3.6	3.6	3.6	2.5
Feed/steam, wt	2.0	2.0	2.0	2.0	1.0	1.0	1.0	1.0	5.0
Run time, min	60	60	65	60	60	60	50	60	60
				Product distribution, wt%					
Organic distil.	53.7	56.0	59.0	50.9	50.3	54.1	56.4	39.6	46.3
Residual oil	4.1	2.4	2.0	7.7	28.2	9.5	9.6	21.8	3.7
Water	15.3	15.9	15.5	14.3	11.9	12.3	13.0	13.9	16.9
Gas	19.1	20.9	21.5	22.2	5.3	14.9	19.8	22.3	19.9
Coke	7.5	4.6	1.7	2.1	1.3	2.7	0.5	0.6	13.0
Unaccounted	0.3	0.2	0.3	2.8	3.0	6.5	0.7	1.8	0.2
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

distilled at 200°C under a vacuum of 172 Pa (corresponding to 450°C at atmospheric pressure) to separate the unreacted oil. The organic distillate was analyzed by gas chromatography using a capillary column and a flame ionization detector. Since tetralin was non-reactive under the experimental conditions, the distillate analysis was performed by subtracting the amount of tetralin fed to the reactor from the total amount of the organic distillate collected. The aspect of tetralin recovery from the products was not studied. The heavy fraction, which constituted less than 20 wt% of the organic distillate, could not be analyzed. For gas analysis, different packed columns and a thermal conductivity detector were employed. A part of the oil remained as coke on the catalyst. It was estimated by regenerating the spent catalyst in air at 600°C for 1 h.

Results and discussion

Overall material balance

The overall material balances obtained during the upgrading of crude tall oil/tetralin feed with and without co-feeding steam are presented in **Tables II and III.** Most of the runs were terminated after a period of 1 h even though the catalyst was still active as indicated by the rate of gas production. In almost all the runs, the material balance was better than 95%. The conversion of tall oil varied between 92 wt% and 97 wt% with or without steam addition at a WHSV of 2.5 h^{-1}. At 3.6 h^{-1} WHSV, the conversion decreased and varied from 86 wt% at 370°C to 95 wt% at 405°C and decreased further upon steam addition. In the latter case where the feed/steam ratio was 1, the conversion was 72 wt% at 370°C but increased to 90 wt% at 390°C before decreasing to 78 wt% at 405°C. The reason for a lower conversion at 405°C is not clear at this time.

The amount of organic distillate varied within a narrow range of 48 wt% to 58 wt% of the total product, and no significant trend with temperature or space velocity was found. When steam was used as the co-feed, the amount of organic distillate decreased in most cases, except at 380°C and 390°C and 2.5 h^{-1}, where it increased to 56 wt% and 59 wt% compared to 54 wt% and 48 wt% in the absence of steam. It is interesting to note that a maximum amount of 58 wt% of organic distillate was obtained at 390°C, as shown in Tables II and III. The fraction of tall oil converting to coke was below 8 wt% in all except one experiment. The amount of coke decreased at higher temperatures. It is remarkable that the conversion to coke in the presence of steam was lowest at about 0.6 wt% at 390°C and 405°C, where the amount of organic distillate was highest. In practice, this would imply a run time extending over several hours. The beneficial role of steam in reducing coking was possibly due to a partial suppression of coke forming reactions or due to partial gasification of coke by steam (*21*). The major effect of increasing the temperature was to increase the conversion to gas product, which was between 15-23 wt% of the total product in most cases, as Tables II and III indicate.

Liquid product composition

The liquid product consisted of unconverted oil, water, and the organic distillate fraction. The fraction of tall oil remaining unconverted was between 2-14 wt% with tetralin but 2-28 wt% when both tetralin and steam were used as diluents. Typically, 13-16 wt% of the oil was converted to water. The composition of the organic distillate is presented in **Tables IV and V.** It consisted of both aliphatic and aromatic hydrocarbons, with the aromatics around 76-88 wt%. Among these aromatic hydrocarbons, toluene and xylenes were the major components, with concentrations of 17-29 and 20-33 wt% respectively. Benzene and ethyl benzene were between 6-23 and 5-13 wt%. Between 6-20 wt% of the organic distillate consisted of a heavy fraction, except at 370°C, 3.6 h^{-1} WHSV, when its concentration was 34 wt%. The components of the heavy fraction, which amounted to a maximum of 17 wt% of the organic distillate, as shown in Table IV, could not be identified.

In the presence of steam, the concentration of aromatic hydrocarbons decreased, varying between 61-74 wt% of the organic distillate at 2.5 h^{-1} and 34-74 wt% at 3.6 h^{-1}, as shown in Table V. Benzene, toluene, xylenes, and ethyl benzene were still the main components, with a total concentration of 34 to 71 wt% of the organic distillate.

IV. Composition of organic distillate from tall oil-tetralin experiments

Run no.	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*
Temperature, °C	370	380	390	405	370	380	390	405
Space velocity, h^{-1}	2.5	2.5	2.5	2.5	3.6	3.6	3.6	3.6
Composition, wt%								
C_5	...	1.2	0.5	1.0	...	0.9	2.6	...
C_6	0.2	1.6	1.0	1.9	0.5	1.0	1.9	...
C_7	0.2	0.9	0.6	0.5	0.4	0.6	0.8	0.1
C_8	0.2	0.2	0.3	0.1	...	0.1	0.3	0.2
C_9	8.6	1.4	5.3	6.0	2.0	7.2	7.4	6.4
C_{10}	5.7	4.8	4.2	0.1	4.9	4.0	3.9	2.8
Total nonarom.	14.9	10.1	12.3	14.8	7.8	13.8	16.9	9.5
Benzene	6.5	13.6	14.9	23.7	14.5	12.6	14.6	4.0
Toluene	21.2	23.0	23.8	29.4	23.3	22.2	23.2	26.0
Ethyl benzene	8.5	7.5	7.3	9.4	8.4	7.2	5.6	13.5
m, p Xylene	19.4	17.4	17.5	19.1	18.3	16.8	17.0	26.7
O-Xylene	5.5	4.7	4.8	5.5	4.7	4.4	3.4	7.0
C_9 aromatic	3.8	9.4	4.1	1.4	9.7	2.8	4.6	5.7
Total aromatics	64.9	75.6	72.4	88.5	78.9	66.0	68.4	82.9
Heavy fraction	16.4	9.6	12.6	...	12.7	17.2	12.6	5.8
Unaccounted	3.8	4.7	3.1	1.9	0.6	3.0	2.1	1.8
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

V. Composition of organic distillate from tall oil-tetralin experiments in the presence of steam

Run no.	*9*	*10*	*11*	*12*	*13*	*14*	*15*	*16*	*17*
Temperature, °C	370	380	390	405	370	380	390	405	380
Space velocity, h^{-1}	2.5	2.5	2.5	2.5	3.6	3.6	3.6	3.6	2.5
Composition, wt%									
C_5	1.0	1.4	1.0	0.8	...	...	2.7	2.2	0.9
C_6	1.3	1.5	2.3	1.0	...	0.1	1.5	1.6	1.2
C_7	1.8	1.0	0.8	0.7	0.4	0.4	1.4	1.5	0.7
C_8	0.7	4.2	2.0	0.5	...	0.5	0.5	0.6	0.1
C_9	8.2	6.0	4.8	7.3	22.0	10.7	10.2	9.7	7.2
C_{10}	4.4	5.2	5.3	3.8	7.4	3.4	14.4	5.2	4.0
Total nonarom.	17.4	19.3	16.2	14.2	29.8	15.2	30.8	20.8	14.1
Benzene	12.3	8.2	7.4	10.1	1.4	6.7	6.0	9.6	12.9
Toluene	21.0	19.6	21.3	22.1	10.4	29.4	16.4	24.8	21.2
Ethyl benzene	7.8	6.5	7.0	6.4	5.7	11.0	5.9	8.0	6.8
m, p Xylene	15.8	17.8	19.6	18.7	14.5	17.9	16.2	21.8	16.0
O-Xylene	4.0	3.0	3.3	3.8	1.0	6.6	1.7	3.2	4.4
C_9 aromatic	2.5	6.7	5.5	3.2	1.9	2.3	2.6	3.6	2.5
Total arom.	63.4	61.8	64.1	64.5	34.9	74.1	48.9	71.1	63.8
Heavy fraction	17.0	18.7	17.5	19.5	34.3	7.7	17.7	6.5	16.3
Unaccounted	2.2	0.2	2.2	1.7	0.9	3.0	2.6	1.6	5.8
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

VI. Composition of gas product from tall oil-tetralin experiments

Run no.	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*
Temperature, °C	370	380	390	405	370	380	390	405
Space velocity, h^{-1}	2.5	2.5	2.5	2.5	3.6	3.6	3.6	3.6
Composition, wt%								
Methane	1.4	1.3	1.8	2.2	1.6	1.7	1.7	1.6
Ethylene	2.3	3.1	5.2	3.7	3.4	4.1	5.2	5.0
Ethane	0.9	1.0	1.6	1.6	1.1	1.3	1.1	1.4
Propylene	3.8	5.7	9.5	7.0	6.4	7.1	9.8	9.4
Propane	48.4	47.0	42.8	47.2	43.1	47.3	41.7	42.7
n-Butane	27.2	26.5	20.3	23.3	22.1	23.6	23.6	21.5
1-Butene	1.0	1.8	2.6	1.8	1.8	2.0	3.0	2.4
Isobutylene	9.5	9.8	9.0	9.6	8.4	9.2	9.9	8.9
n-Pentane	2.9	3.0	2.3	2.6	2.3	2.6	2.9	2.3
1-Pentene	0.4	0.5	0.5	0.5	0.4	0.5	0.7	0.5
C_6	0.02	0.04	0.02	0.1	0.01	0.03	0.04	0.02
CO	1.7	...	3.2	...	8.3	...	...	3.4
CO_2	0.01	0.01	...	...	0.06	...	0.01	0.02
Unaccounted	0.5	0.3	1.2	0.4	1.1	0.6	0.4	0.9
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Gas product composition

The composition of the gas product is shown in **Tables VI and VII.** Among the gaseous components, propane alone contributed between 41 wt% and 48 wt%, followed by n-butane with a concentration of 19-27 wt%. The olefin/paraffin ratio was 0.2-0.4. In all the cases, the concentration of CO_2 was vanishingly small and the concentration of CO was highest at 8.3 wt%. Upon steam addition, the olefin/paraffin ratio varied between 2-15. The highest value for this ratio was 15 at 390°C and 3.6 h^{-1} WHSV. In these experiments, propylene was the single largest component, representing 27-48 wt% of the product which still contained significant amounts of propane and butane (3-35 wt% combined) and 8-15 wt% each of ethylene and butenes. These results show that the waste tall oil may be used as an excellent source of olefinic fuels such as ethylene and propylene as well as propane or butane. The concentration of CO in the presence of steam increased and was highest at 15 wt%.

The above product distributions indicated that the amount of water formed during the catalytic conversion of crude tall oil over HZSM-5 varied from 11-16 wt% of the total product. The amount of gas product varied from 10 wt% to 24 wt% and the concentrations of CO and CO_2 in the gases were rather small. Since the components of the coke and the heavy fraction of the organic distillate could not be analyzed, a complete oxygen balance was difficult. However, it seems that most of the oxygen in the tall oil ends up as water.

Fuels from tall oil

This study has clearly shown that the crude tall oil may be converted selectively to the desired hydrocarbon products by using HZSM-5 catalyst and co-feeds such as tetralin and steam. This suggests a new route for the manufacture of fuels and desired chemicals using essentially a waste stream of the kraft pulp industry. Also, in this process no de-pitching of the crude tall oil is necessary. It involves the use of a HZSM-5 zeolite as the catalyst and the operation at an atmospheric pressure and moderate temperatures between 370°C and 405°C. The problems of catalyst deactivation are minimal. The catalyst can be regenerated easily by heating with air for 1 h at 600°C. The major products which can be produced by this process include liquid fuels with 60-75 wt% concentration of aromatic hydrocarbons. Alternately, benzene, toluene, and xylenes may be recovered, since their highest concentrations in the distillate were around 12, 29, and 25 wt% respectively. The amount of gas product varied from 14 wt% to 22 wt% of the total product and should be an excellent source of gaseous fuels or olefins under suitable operating conditions.

Conclusions

1. Extremely high conversions (over 90 wt%) of crude tall oil were obtained over HZSM-5 catalyst in the temperature range of 370°C to 405°C.
2. The highest conversion to organic distillate was 58 wt% of the feed and it contained over 80 wt% aromatic hydrocarbons.

VII. Composition of gas product from tall oil-tetralin experiments in the presence of steam

Run no.	*9*	*10*	*11*	*12*	*13*	*14*	*15*	*16*	*17*
Temperature, °C	370	380	390	405	370	380	390	405	380
Space velocity, h^{-1}	2.5	2.5	2.5	2.5	3.6	3.6	3.6	3.6	2.5
Composition, wt%									
Methane	0.8	0.4	0.2	0.2	0.3	0.2	0.1	0.1	1.4
Ethylene	9.3	10.4	16.4	15.1	15.3	15.0	11.6	13.1	3.5
Ethane	0.6	0.4	0.1	0.2	0.2	0.2	0.1	0.1	1.1
Propylene	27.4	28.4	44.6	38.8	39.7	46.3	47.8	47.3	6.1
Propane	23.2	17.0	5.2	8.7	9.1	6.9	2.7	3.7	46.8
n-Butane	13.9	11.0	4.4	7.2	6.6	5.9	1.7	2.6	25.9
1-Butene	9.4	8.0	11.2	10.2	11.7	13.7	14.2	12.2	1.9
Isobutylene	6.3	7.1	6.5	6.6	7.9	6.4	6.9	6.5	9.5
N-Pentane	2.9	1.6	0.9	1.2	1.7	1.5	0.8	1.4	2.8
1-Pentene	0.6	0.5	0.7	0.5	1.1	1.1	0.8	0.7	0.5
C_6	0.03	0.03	0.02	0.01	0.6	...	...	...	0.06
CO	4.5	14.3	9.6	11.3	6.0	2.8	13.0	11.7	0.3
CO_2	0.01	0.01	0.01	...	...	...	0.01	0.01	0.02
Unaccounted	1.1	0.9	0.2	...	...	...	0.3	0.6	0.2
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

3. Usually 15-23 wt% of the oil was converted to gaseous product containing paraffinic hydrocarbons. With steam as cofeed, the gas product consisted mostly of C_2 to C_5 olefins.
4. Usually coke formation was around 5 wt%. However, with steam as cofeed, coke formation decreased drastically and was about 0.5 wt% at 390°C and 405°C.□

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