

HYDROGENATION/DEHYDROGENATION REACTIONS OF ROSIN

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INTRODUCTION

One of the most important factors controlling the high-temperature thermal stability of jet fuels is their chemical composition [1]. At high temperatures, pyrolysis reactions of certain components in the fuel become significant and result in the formation of gums and insoluble solids. These materials will reduce heat transfer efficiency, degrade valve performance and deposit solids in the fuel pipeline and in fuel combustor nozzles. Cycloalkanes are desirable components of advanced jet fuels because of their high thermal stability. If cycloalkanes can be produced in high yield by direct coal liquefaction, downstream processing of the product would be reduced. In order to obtain a high quality product, selection of a good feedstock is vital. Therefore, if cycloalkanes are to be produced from coal, it is reasonable to choose coals with high concentrations of these compounds already present or structures that could be easily converted to cycloalkanes.

The higher plants contain terpenoid-based substances commonly known as resins. These resins may polymerize on exposure to air, and the polymerization *in situ* in dead plants gives rise to the resinite maceral found in almost all coals. Several recent publications on resins in coal [2-6] have indicated that the resins are composed of oxidatively polymerized sesquiterpenoids and diterpenoids. Certain coals from Canada, the Far East and Australia contain diterpenoid resinites in high concentration. Western United States coals contain sesquiterpenoid resinite in high concentration (up to 5wt%) [5,6]. This paper will deal with modeling of diterpenoid resinite reactions, although the results obtained do have some relevance to sesquiterpenoid resinites. If the behavior of resinite under liquefaction conditions can be determined and understood, a highly efficient liquefaction system can be developed. Coals with high resinite concentration can be liquefied, and the cycloparaffinic products from resinite can be extracted into the oil fraction, producing liquids that are thermally stable and could be a source of high-quality jet fuel. However, because resinite is a complex mixture of polymerized compounds, it is advisable to study model compounds. This makes analysis of products easier and evaluation of reaction pathways less complicated. Rosin is commercially available and contains 90% diterpenoids (isomeric with abietic acid). In a sense, rosin is a simplified analogue of certain resinite structures and its hydrogenation-dehydrogenation behavior should give an insight into resinite liquefaction.

Because of the dwindling supply of petroleum and the possible environmental effects of fossil fuel conversion, alternative fuel sources have been sought. Biomass has emerged as a possible alternative to produce liquid fuels and chemicals. The environmental effects of the conversion of biomass should be less than those of fossil fuels. With careful process development and investigation into the chemistry of biomass conversion, the use of this renewable energy source should be realized. Tall oil is a by-product of the Kraft wood-pulping process. It contains fatty acids and rosin acids in approximately equal proportions. The use of tall oil to produce liquid fuels has been discussed in the literature [7,8] although the chemistry of the hydrocracking of the rosin acids has not been addressed. To maximize efficiency of a process to produce fuel components from tall oil or rosin, it is necessary to investigate the hydrocracking behavior of the rosin acids.

This paper will discuss the aromatisation/cracking/isomerisation reactions of rosin compounds with various catalysts. The relevance of these reactions to jet fuel production and biomass conversion will be discussed.

EXPERIMENTAL

Rosin was hydrogenated under different conditions with NiMo/Al₂O₃, Ni-Y zeolite and ammonium tetrathiomolybdate. All reactions were carried out in 25ml capacity microautoclave

reactors with cold hydrogen pressure of 7MPa. The reactors were brought to the desired temperature using a preheated sandbath. The products were analysed by GC/MS using a HP5890A GC with 5971A mass selective detector and quantified using heptadecane as an external standard.

RESULTS AND DISCUSSION

Figure 1 shows the concentration of reaction products and how they vary with temperature. At 350°C the major products of reaction are tricyclic compounds, e.g. norabietatriene. This compound is formed by decarboxylation and dehydrogenation of abietic acid (a major component of rosin). Norabietatriene is further dehydrogenated to tetrahydrotene and retene. At this low temperature, only a small amount of retene is formed. Cracking of the 3-ring compounds is minimal, with only C₄-benzene and isopropyltetralin being formed in large concentration.

At 400°C the concentration of norabietatriene increases with increasing dehydrogenation/decarboxylation of abietic acid. This increase also yields an increase in tetrahydrotene and retene in the reaction products. The concentration of alkylbenzenes triples in the products at the higher temperature. This can be accounted for by cracking of the saturated ring of isopropyltetralin seen at 350°C. The concentration of naphthalenes has not increased. This is because the temperature is not yet high enough for major cracking of the 3-ring compounds. In theory, cracking of norabietatriene will occur at the saturated terminal ring, as in hydrogenated phenanthrene, giving naphthalenes [9,10]. This does not occur at 400°C.

At 450°C naphthalenes and benzenes are now being formed. These naphthalenes are cracking products of norabietatriene, tetrahydrotene, and other partially saturated 3-ring compounds. It is unlikely that the fully aromatic retene has cracked. It is widely held that all hydrocracking reactions go in two stages: first, hydrogenation of the terminal ring and then cracking of the saturated ring [10]. Figure 1 shows the concentration of norabietatriene and tetrahydrotene decreasing after 400°C. This is in line with the thoughts that it is these compounds that are cracking to benzenes and naphthalenes, and not retene, which continues to increase.

If we interpret the chromatograms purely from the point of view of wanting to produce a good quality jet fuel, it appears that hydrocracking of the tricyclic compounds is the route to take. Naphthalenes and benzenes are produced by cracking of the diterpenes in rosin. These compounds can form the "backbone" for subsequent hydrogenation to produce desirable cycloalkanes and tetralins. Unfortunately these cracking reactions occur at high temperatures, which is accompanied by increasing dehydrogenation of the cycloparaffinic diterpenoids. In a sense, we are destroying the major property of these compounds that they were selected for — their cycloparaffinic nature. The fully aromatic retene seen in large concentration at 450°C will give rise to solid deposits in thermally stressed jet fuel. The reaction at 500°C has almost totally cracked the 3-ring compounds in rosin to naphthalenes and benzenes. Cleavage of side chains has also occurred. This may seem a good reaction if jet fuel is to be produced, but the amount of dehydrogenation makes the feasibility of this reaction being of any use small. Continuing work may prove otherwise; i.e., is it possible to re-hydrogenate the aromatic compounds to compounds that are desirable and can be hydrocracked? It is likely that in going to such a high temperature, we are simply 'going backwards to go forwards'.

Figure 2a shows how the concentrations of the products vary with reaction time for the non-catalytic run. It can be seen that cracking does not occur to a great extent until after 30 minutes. This is simultaneous with the disappearance of norabietatriene and tetrahydrotene. The concentration of retene continues to increase even as the concentration of naphthalenes increases from 0.4-3.6 mg/ml. This is further evidence that retene does not crack, although its concentration may be kept down due the fact that tetrahydrotene is being hydrocracked. To produce thermally stable cycloalkanes from diterpenoid structures, it is necessary to hydrocrack the 3-ring compounds to naphthalenes and benzenes. This needs a high temperature which also promotes dehydrogenation of cycloparaffinic compounds to unwanted fully aromatic compounds. Therefore, a two stage reaction is envisaged: 1) A high temperature cracking reaction to yield a 'backbone' of naphthalenes and benzenes. This means a reaction temperature of at least 450°C, and maybe as

high as 500°C, and a reaction time of at least 45 minutes. 2) A low temperature hydrogenation stage. The naphthalenes and benzenes from stage 1 would be catalytically hydrogenated to cycloalkanes and tetralins. The final products should fall into the jet fuel boiling range, yielding a highly thermally stable fuel.

In order to establish the optimum conditions for a temperature-staged catalytic hydrogenation, the product distribution of rosin hydrogenation was investigated using three catalysts: NiMo/Al₂O₃, Ni-Y(zeolite), and ammonium tetrathiomolybdate (ATTM).

Figure 3 shows a histogram of the product distribution of rosin hydrogenation with various catalysts (reaction temperature 400°C, reaction time 60 min.). All three of the catalysts caused a major reduction in the concentration of retene. ATTM did not crack the tricyclic compounds in rosin. In fact, it can be seen that the non-catalytic run produced more benzenes than the run with ATTM. This can be explained by the formation of dehydroabietane in the ATTM experiment. This compound is more stable than norabietatriene, due to the methyl-group substitution of the carboxyl group. Therefore, dehydroabietane does not crack and shows less tendency to dehydrogenate. Because of the low hydrocracking effectiveness of ATTM it was decided not to continue with this catalyst in this investigation. Supported NiMo shows good hydrocracking effectiveness and the Ni-Y catalyst shows an even greater cracking capability. This preliminary investigation into catalytic reactions of rosin led into a more detailed look at how product distribution would vary with time. This would help in determining the best temperature program for the two-stage reaction postulated previously.

Figure 2b shows the product distribution vs time for rosin hydrogenation with NiMo at 450°C. Three major points arise from this graph: 1) From 5-60 minutes, there is no overall increase in retene, but after 20 minutes, methylphenanthrene is formed by dehydrogenation/dealkylation of tetrahydrotetene. 2) The major cracking reactions occur after 10 minutes. Secondary cracking of naphthalenes to benzenes occurs after 20 minutes. This can be seen by the increase in concentration of benzenes after 20 minutes but naphthalenes show a 'slowing down' of formation. 3) After 40 minutes there is a maximum in the benzenes concentration. This could be explained two ways—formation of gases or coking of the catalyst. The appearance of methylphenanthrene tends to support the latter explanation but dealkylation would lead to hydrocarbon gas formation.

1-Methyl-4-isopropylbenzene (p-cymene) reaches a maximum in concentration at 40 minutes. Toluene increases slowly throughout the reaction times. The isopropyl group is quite stable but will be cleaved after 40 minutes at 450°C. This could also explain the decrease in benzenes concentration seen in Figure 2b. This is due to C₂-C₃ hydrocarbon gases being produced by cleavage of side chains. Isopropyltetralin reaches a maximum at approximately 30 minutes. The disappearance of isopropyltetralin is simultaneous with the increase in concentration of methylindene. This is due to dealkylation/isomerisation of isopropyltetralin.

As mentioned in the introduction, this work does have some application to sesquiterpenoid resinite. The proposed pathway of dealkylation to tetralin would probably occur in sesquiterpenoid structures. The isomerisation reaction could probably be controlled by tailoring the reaction temperature, and the possibility of producing tetralin is good.

Figure 2c shows the product distribution of rosin hydrogenation vs time with Ni-Y catalyst at 450°C. It can be seen that after 10 minutes of reaction, the tricyclic compounds in rosin have almost totally been cracked. Benzenes, naphthalenes and indenenes are produced in high concentration and continue to increase up to 60 minutes of reaction. Isopropyltetralin is completely dealkylated and isomerized after 60 minutes. The isomerisation reaction seems to be the major cause of loss of isopropyltetralin. This was observed with the simultaneous increase of dihydromethylindene. p-Cymene is dealkylated to toluene after 10 minutes of reaction.

In order to find a relationship between the cracking of tricyclic compounds and the appearance of mono and bicyclic compounds, a plot of the ratio of 1+2 ring to 3-ring compounds is shown in Figure 4. It can be seen that Ni-Y is the most effective hydrocracking catalyst. The maximum at 20 minutes is probably due to secondary cracking of side chains producing gases or coke formation on the catalyst. This would cause a decrease in the calculated ratio. This result also suggests a reverse-temperature-stage-program would be effective in this situation. Most of the

cracking of 3-ring compounds has taken place in the first 20 minutes at 450°C. Therefore, to continue at this high temperature would give no effective increase in the components desired for a high-quality jet fuel, and would cause excess gas formation and an increase in aromaticity.

From the above results, reaction pathways have been proposed (Scheme 1 and 2). Scheme 1 shows the dehydrogenation pathway of abietic acid in rosin. Scheme 2 deals with the possible route of cracking and isomerisation of the 3-ring compounds.

CONCLUSIONS

Diterpenoid compounds can be successfully hydrogenated and cracked to cycloalkanes and hydroaromatics using supported NiMo and Ni-Y catalysts. With careful tailoring of the process temperature and time of reaction, high quality distillate could be obtained. A reverse temperature-staged reaction with optimum conditions chosen from the plots of product distribution could yield maximum concentration of cycloalkanes and hydronaphthalenes. Fully aromatic compounds would be kept to a minimum. Diterpenoids are the most common resins in the geosphere. As well as appearing in some coal resinates, they can be found as ambers or as modern pine resins, e.g. rosin. Their chemical properties can be used in developing high quality fuels, either by direct hydrocracking or as a blending additive in a coal liquefaction process. Some of the reactions occurring in rosin hydrocracking, e.g. dealkylation and isomerisation of substituted tetralins, could be useful in determining the best way to study the liquefaction behavior of sesquiterpenoid resinates, e.g. as found in some Utah coals.

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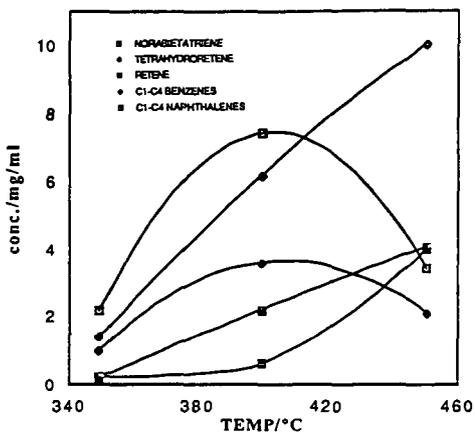


Fig.1 Concentration vs temp:no catalyst

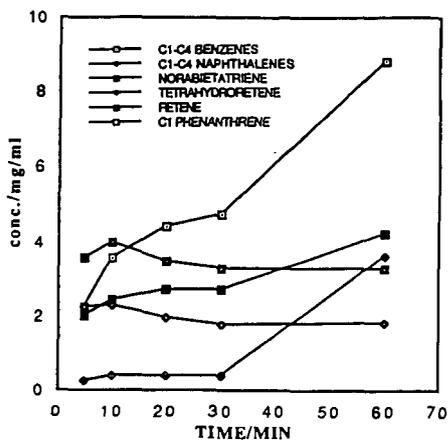


Fig.2a Concentration vs time:no catalyst

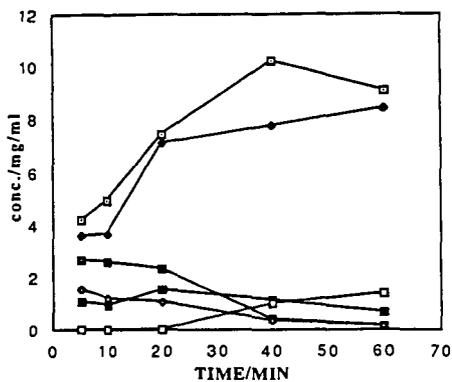


Fig.2b Concentration vs time: NiMo

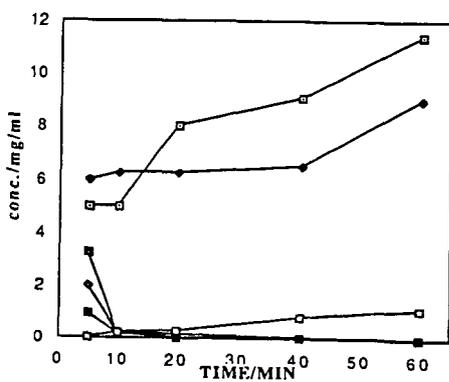


Fig.2c Concentration vs time: Ni-Y

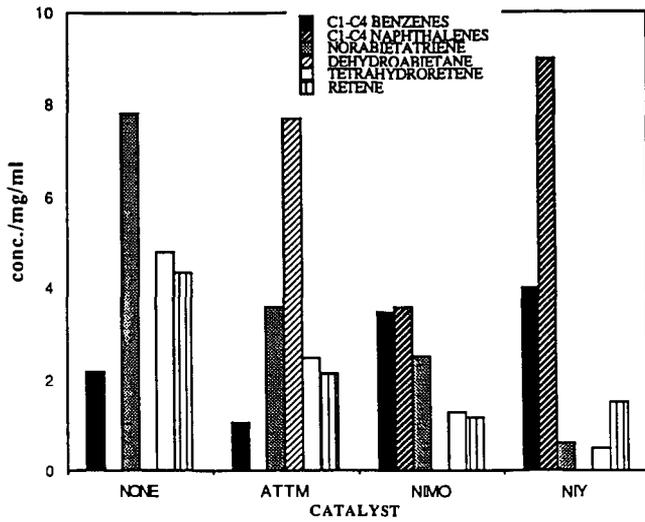


Fig.3 Concentration vs catalyst : 400°C

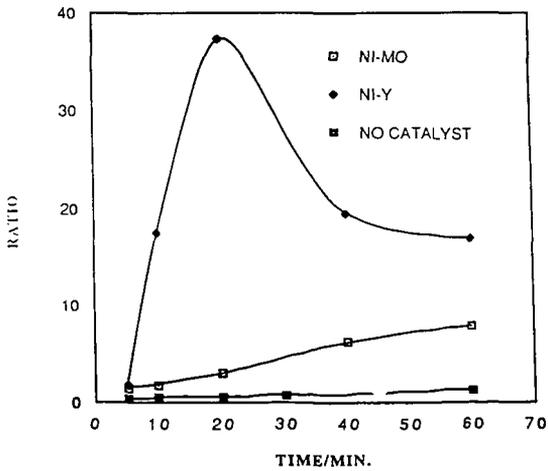


Fig.4 1+2 ring/3-ring compounds vs time

