

## Catalytic Hydrocracking of Waste Vegetable Oil Using High Pressure Flow Apparatus to Obtain Jet Fuel Range Alkanes

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**Summary:** The hydrocracking of waste vegetable (cooking) oil was studied over two different catalysts as an alternative way to produce jet fuel range alkanes (C<sub>9</sub> – C<sub>15</sub>). Experiments were carried out in a packed bed reactor at temperatures of 400, 425 and 450°C and with a hydrogen pressure of 120 bar. Two types of fresh and regenerated catalyst were used: ruthenium/alumina (Ru- $\gamma$ - Al<sub>2</sub>O<sub>3</sub>) and nickel oxide/alumina (NiO- $\gamma$ - Al<sub>2</sub>O<sub>3</sub>), both subject to a sulphidation pre-treatment prior to the experimental run. At the conditions studied, the hydrocracking on fresh NiO- $\gamma$ - Al<sub>2</sub>O<sub>3</sub> catalyst at the highest temperature gave the highest concentration on a mass basis (7.14 wt. %) of C<sub>9</sub>-C<sub>15</sub> hydrocarbons in the liquid product. The liquid product yield ranged from 29.83 to 92.06 wt. %. The higher yields were obtained at the higher reaction temperatures using fresh catalyst. Within the liquid product, the higher percentages of C<sub>9</sub> – C<sub>15</sub> alkanes were achieved at the higher temperatures using fresh catalyst, indicating that an increase in reaction temperature favours hydrocracking. Furthermore, fresh catalyst proved to have a greater effect on the degree of hydrocracking when compared to its regenerated counterpart. Fresh untreated catalyst proved less effective than regenerated treated catalyst indicating the importance of the pre-treating stage in order to activate the catalyst for hydrocracking of triglycerides. The balance of the product was made up of gas and a waxy residue. This waxy residue was found to contain a small portion of similar alkanes to those in the liquid product but would require further processing to separate out the target compounds from the high molecular weight hydrocarbons.

Keywords: Jet fuel range alkanes, Hydrocracking, Waste cooking oil, Packed bed reactor.

### Introduction

#### *Study Motivation*

In recent years, investigation into an alternative source of transportation fuel has become increasingly important due to the rapid depletion rate of crude oil reserves [1]. Furthermore, emphasis has been placed on finding a fuel that is renewable, environmentally friendly and has a lower production cost than current petroleum processing methods. A potential alternative source is provided by vegetable oils obtained from renewable plant seed extracts. Fuels derived from this source are considered environmentally friendly, and are one example of biofuels. Biofuels are cleaner burning in that their use results in little to no sulphur emissions. Since these plants require carbon dioxide (CO<sub>2</sub>), a greenhouse gas, to grow, the CO<sub>2</sub> emissions produced by the burning of biofuels do not add to the current CO<sub>2</sub> level in the atmosphere [1]. In an attempt to further reduce production costs, some investigations have focused on the use of waste cooking oil as a feedstock. This can be obtained from local restaurants at a significantly lower price than virgin cooking oil.

Many countries have established rigid government regulations and full or partial tax exemption to promote utilization of biofuels [2]. The EU has set the carbon penalties in order to decrease the environmental pollution. Airlines are required to use a blend of 50% bio-jet fuel by the year 2020. Failure to do so will result in European Union (EU) carbon penalties. This encourages companies to invest in research for efficient biofuels production processes. The selected process conditions for this study were based on the associated literature. At the time this study was undertaken, there was limited published data on this type of research. Most reviewed literature focuses on using triglycerides as a feedstock to obtain *n*-alkanes in the diesel range (C<sub>14</sub>-C<sub>20</sub>) as it requires a smaller degree of cracking and less energy while still producing substantial yields.

#### *Hydrocracking Theory*

Triglycerides make up the structure of all vegetable oils and fats found in nature. They usually contain a linear chain of 12 to 24 carbon

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atoms [3]. Cooking oil contains many triglyceride compounds. The composition of fatty acids in waste cooking oil contains large amounts of Linoleic acid and Oleic acid (43.85 and 33.75% respectively) while the remainder is made up of Linolenic acid, Palmitic acid and Stearic acid [4].

The reactions in this study include both hydro treating and hydrocracking. Hydro treating involves the conversion of unsaturated compounds into saturated compounds [2]. Hydrocracking is characterized by the breaking of long chain saturated compounds into smaller compounds [3]. Based on analytical results many authors have theorized mechanisms for the hydrocracking of cooking oil. It is generally acknowledged that the reactions that take place include decarboxylation, decarbonylation, reduction (hydrodeoxygenation) and hydrogenation. Predominant hydro-converted products are *n*-alkanes ranging from C15 – C18. Expected by-products are carbon monoxide, carbon dioxide and water. Hydro processing is energy intensive hence a catalyst is essential to significantly decrease the activation energy required for the hydro treating and hydrocracking reactions to occur. A variety of different catalysts, both sulphur free and pre-treated with sulphur, have been successfully used to convert cooking oil into straight chain alkanes. The catalysts utilized in this study were ruthenium/alumina (Ru- $\gamma$ - Al<sub>2</sub>O<sub>3</sub>) and nickel oxide/alumina (NiO- $\gamma$ - Al<sub>2</sub>O<sub>3</sub>). Characterization studies of these hydroprocessing catalysts, performed under working conditions, indicate that they are active as metal sulphides and hence require sulphur pre-treatment prior to the experimental run [5]. In the catalytic cracking of petroleum fractions, carbonaceous materials gradually accumulate on the surface of the catalyst. This material lowers the catalyst activity and needs to be periodically burned off [6].

#### *Aim and Objectives*

The major aim of this work was to break down waste cooking oil (triglyceride molecules) into *n*-alkanes, with focus on obtaining C11-C13 saturated hydrocarbons, the typical constituents of aviation fuel. This was performed via a high pressure catalytic hydrocracking process. Also the effect of pre-treatment and regeneration on the efficiency of the hydrocracking catalysts was determined.

The objectives included studying the effect different process conditions had on the mass fraction of C9-C15 saturated hydrocarbons in the liquid product. The variables under investigation were the reaction temperature, and the type of alumina based catalyst. The effectiveness of catalyst regeneration on re-establishing hydrocracking activity was also quantitatively assessed.

#### **Experimental**

##### *Pre-Run Procedures (Experimental Setup and Catalyst Pre-Treatment)*

Catalyst particles with an average diameter of approximately 3 mm were used in this work. A 1cm diameter stainless steel reactor tube was packed using spherical glass beads at either end, while the catalyst occupied the central region. A steel mesh of 1 mm diameter was inserted at the bottom of the reactor to prevent glass beads and/or catalyst particles from being carried out the exit line. The packed reactor was placed into the reactor heater unit. Fig. 1 shows a schematic of the experimental setup.

For the catalyst pre-treatment procedure, hydrogen gas (2 bar) and hydrogen sulphide gas diluted in nitrogen (1 bar) were passed through the reactor bed in a ratio that diluted the sulphur content from 0.05 to 0.02 vol. %. The process was started at room temperature and ramped up to 400° C at a rate of 5° C per minute where it was held for 10 h.

##### *Experimental Run Procedure*

Upon completion of the catalyst pre-treatment, reactant hydrogen gas at 120 bar was passed through the reactor while the reactor bed was heated to the reaction temperature. Once at the required reaction temperature (400, 425 and 450° C), the waste cooking oil was pumped at 0.1 ml/min for a duration of 2 h from the storage tank into the reactor. The liquid and waxy products formed were collected in a glass vessel while the gaseous products were passed through a gas analyser or vented. Exit gas flow rate was continuously monitored using a bubble flow meter. After the 2 hour run, system pressure was released via a valve on the exit line, and the products were taken for sample preparation and analysis.

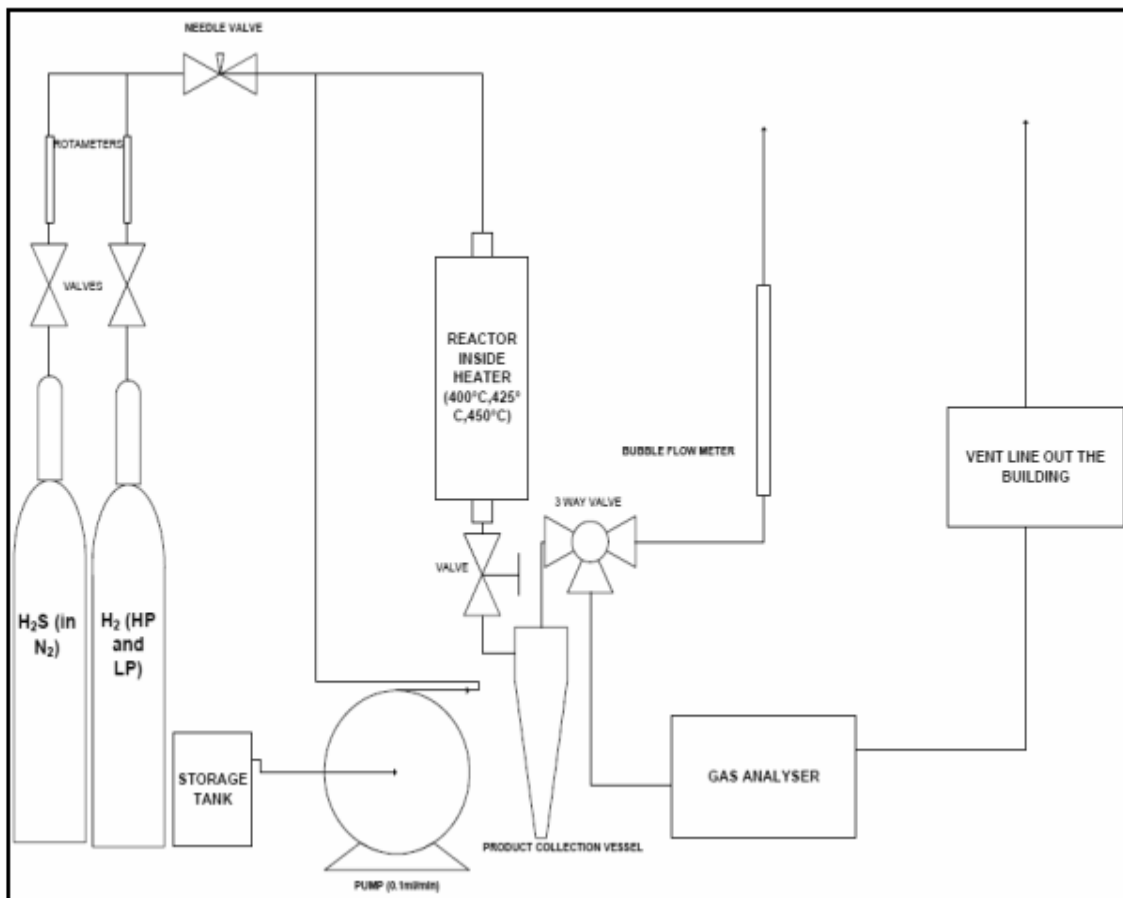


Fig. 1: Experimental Setup (Schematic).

#### *Post-Run Procedures (Product Analysis and Catalyst Regeneration)*

The product was spun in a centrifuge for 3 minutes at 4000 rpm in order to separate the liquid from the waxy residue. The liquid was decanted from the centrifuge vial. Liquid product (approx. 5 drops) was dissolved in xylene (internal standard) for Gas chromatography – Mass spectrometry (GC-MS) analysis. An internal standard method is an area-ratio method which is used to determine the amount of mass of each target compound obtained in the liquid product. The liquid product and xylene masses were recorded in order to perform composition calculations post analysis.

The GC-MS provides qualitative analysis but can be used to perform some quantitative analysis. 1  $\mu$ L of the prepared solution was injected into the GC-MS via an auto injector unit. The resultant total ion chromatogram was used to identify the compounds contained in the liquid product and provide compound peak area values for subsequent calculations.

Catalyst regeneration was performed after 3 experimental runs were conducted at different temperatures using the fresh catalyst. This process required air to be passed through the reactor at atmospheric pressure at a reactor bed temperature of 500 °C. At these conditions, the oxygen in the air stripped off the carbonaceous material that may have formed from the previous experimental runs. Pre-sulphiding was also carried out on regenerated catalysts. Thereafter 3 more experimental runs were performed at the investigated temperatures in order to compare fresh and regenerated catalysts effectiveness.

#### *Product Compounds Yield Calculation*

The total mass fed to the system was determined using the density and volumetric flow rate of the oil over the 2 hour experimental duration. Using an appropriate molar response factor for xylene, the moles of each target compound were calculated via the internal standard method. Thereafter, masses, mass fractions and yields of the target compounds were evaluated.

## Results and Discussion

The major aim of this work was to obtain liquid C<sub>11</sub> – C<sub>13</sub> *n*-alkanes via the high pressure hydrocracking of waste cooking oil over alumina based catalysts. In addition to successfully obtaining the desired compounds, pre-sulphiding and regeneration were performed to assess their effect on the efficiency of hydrocracking catalysts.

### Initial Experimental Work and Troubleshooting

Over a 2 hour run, the expected mass of the oil fed to the reactor was 9.108 g which was used in all subsequent calculations. The volume of the catalyst bed was calculated to be 16.81 cm<sup>3</sup> which resulted in a liquid hourly space velocity (LHSV) of 0.36 h<sup>-1</sup>. The volumetric flow rate is a function of pressure and temperature and since the oil enters the reactor at a much lower temperature than the catalyst bed, this value of LHSV may not be an accurate representation of the real system. The lowest available pump flow rate was selected to ensure the highest possible residence time and hence the greatest achievable degree of cracking.

Based on past literature regarding hydrocracking of cooking oil, a proposed system pressure of 40 bar [7] was utilized. However, this was found to be too low since the product was composed of entirely waxy residue. The system pressure was increased gradually up to about 120 bar, where the product contained less waxy residue and a significant amount of liquid. This also suggests that a greater degree of cracking is achieved at a higher system pressure.

### Data Analysis

The liquid composition from the product obtained ranged from 29.83 to 92.06 wt%. The lower compositions were obtained at the lower temperatures and for the regenerated catalysts. More wax was formed relative to liquid at these conditions. A small amount of liquid product may have been lost as it could have remained entrapped in the waxy residue regardless of the centrifugal separation employed. An important assumption was that the mass fraction of each compound in the sample used for GC-MS analysis was equal to the mass fraction of the respective compounds in the total liquid product.

Tables 1 to 4 contain the calculated results based on the analysis of each liquid sample obtained from the experiments using GC-MS. It was assumed that the mass fraction in the sample vial was equal to the mass fraction in the total liquid product.

Table-1: Mass and mass percentage of C<sub>11</sub>-C<sub>13</sub> obtained using virgin Ru- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

n-Alkanes carbon number	Ru- $\gamma$ -Al <sub>2</sub> O <sub>3</sub> - Virgin					
	400 °C		425 °C		450 °C	
	Mass (g)	Mass (%)	Mass (g)	Mass (%)	Mass (g)	Mass (%)
C <sub>11</sub>	0.017	0.61	0.100	1.38	1.73	2.06
C <sub>12</sub>	0.014	0.51	0.097	1.21	1.44	1.72
C <sub>13</sub>	0.022	0.80	0.127	1.59	1.79	2.14

Table-2: Mass and mass percentage of C<sub>11</sub>-C<sub>13</sub> obtained using virgin NiO- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

n-Alkanes carbon number	NiO- $\gamma$ -Al <sub>2</sub> O <sub>3</sub> - Virgin					
	400 °C		425 °C		450 °C	
	Mass (g)	Mass (%)	Mass (g)	Mass (%)	Mass (g)	Mass (%)
C <sub>11</sub>	0.071	1.32	0.100	1.51	0.221	2.69
C <sub>12</sub>	0.072	1.34	0.080	1.21	0.177	2.15
C <sub>13</sub>	0.097	1.80	0.101	1.53	0.189	2.30

Table-3: Mass and mass percentage of C<sub>11</sub>-C<sub>13</sub> obtained using regenerated Ru- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

n-Alkanes carbon number	Ru- $\gamma$ -Al <sub>2</sub> O <sub>3</sub> - Regenerated					
	400 °C		425 °C		450 °C	
	Mass (g)	Mass (%)	Mass (g)	Mass (%)	Mass (g)	Mass (%)
C <sub>11</sub>	0.023	0.86	0.044	0.95	0.126	1.81
C <sub>12</sub>	0.021	0.78	0.042	0.90	0.117	1.67
C <sub>13</sub>	0.029	1.08	0.054	1.17	0.137	1.96

Table-4: Mass and mass percentage of C<sub>11</sub>-C<sub>13</sub> obtained using regenerated NiO- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

n-Alkanes carbon number	NiO- $\gamma$ -Al <sub>2</sub> O <sub>3</sub> - Regenerated					
	400 °C		425 °C		450 °C	
	Mass (g)	Mass (%)	Mass (g)	Mass (%)	Mass (g)	Mass (%)
C <sub>11</sub>	0.066	1.04	0.088	1.50	0.168	2.40
C <sub>12</sub>	0.048	0.75	0.066	1.14	0.141	2.01
C <sub>13</sub>	0.083	1.30	0.087	1.49	0.158	2.25

The same data is plotted below in form of histograms for easier analysis.

Fig. 2 and 3 compare catalyst effectiveness in terms of mass percentage of C<sub>11</sub> – C<sub>13</sub> *n*-alkanes in the hydrocracking reactions. In both cases, it is observed that the NiO- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst proved more effective than the Ru- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. This is evident as the mass percentages of the target compounds were higher for the NiO- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst at every temperature. It was also observed that at a higher reaction temperature, a higher percentage of target compounds were achieved. This suggests that the cracking reactions are favoured at higher temperatures.

The experimental run at 400° C using virgin Ru- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was not pre-treated. This resulted in a much poorer percentage of target compounds in the liquid product when compared to all other experimental runs which contained pre-treated catalyst.

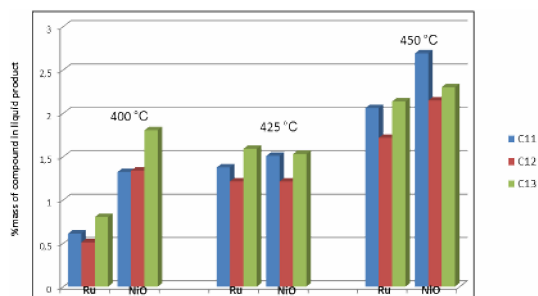


Fig. 2: Comparison of the mass % of C<sub>11</sub>-C<sub>13</sub> *n*-alkanes using virgin catalysts.

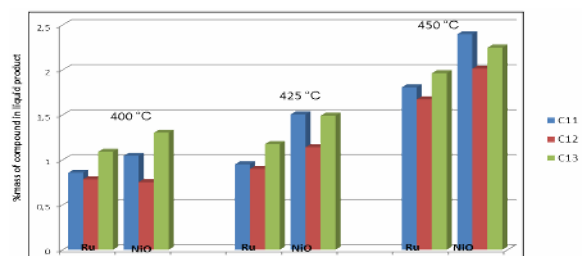


Fig. 3: Comparison of the mass % of C<sub>11</sub>-C<sub>13</sub> *n*-alkanes using regenerated catalysts.

Fig. 4 and 5 allow for the comparison between fresh and regenerated catalysts of Ru- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiO- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> respectively. Five out of the six comparisons indicate a better mass percentage of target compounds using the fresh catalyst. Recall the fresh Ru- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was not pre-treated for the experimental run at 400° C. However, its regenerated counterpart was, and this was the only case whereby the regenerated catalyst performed better than the fresh catalyst. This suggests that the pre-treatment step is vital in order to activate the catalyst for hydrocracking reactions and greatly increases its efficiency.

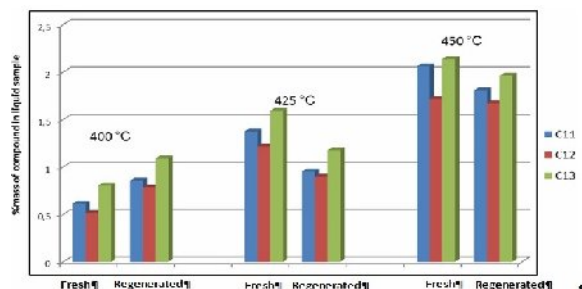


Fig. 4: Comparison of the mass % of C<sub>11</sub>-C<sub>13</sub> *n*-alkanes using virgin and regenerated Ru- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts

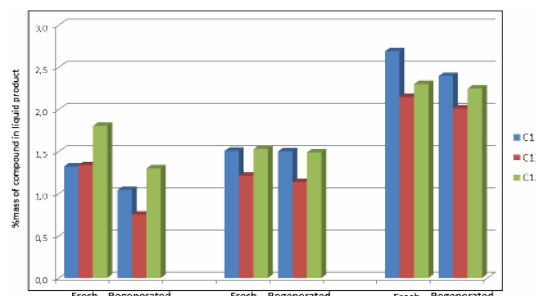


Fig. 5: Comparison of the mass % C<sub>11</sub>-C<sub>13</sub> *n*-alkanes using virgin and regenerated NiO- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts.

The yield of the target compounds ranged from 0.54 to 5.99 wt%. The lowest yield was obtained using the fresh untreated Ru- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst while the highest yield was obtained using fresh pre-treated NiO- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. As expected, the yields followed the same trend as the mass percentage of target compounds in the liquid products for all experimental runs. This serves to consolidate the fact that hydrocracking is favoured at higher temperatures using fresh pre-treated catalyst. The high reaction temperature must be in an appropriate range to sufficiently crack the triglycerides and achieve a desirable degree of hydrogen saturation to ensure the best yield of liquid C<sub>11</sub> – C<sub>13</sub> *n*-alkanes.

Based on all the data and figs, the best conditions for the greatest degree of cracking are obtained when using virgin NiO- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, at the highest reaction temperature of 450 °C.

The system was modified to include the gas analyser in order to observe what gases were being produced. According to the results observed, small amounts of methane, ethane and butane gas were being produced during the hydrocracking process.

## Conclusion

Jet fuel range *n*-alkanes were successfully produced via the hydrocracking of waste cooking oil. The study focused on three typical hydrocracking temperatures over two catalysts, Ru- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiO- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The catalysts were regenerated via high temperature air treatment and re-utilized in the hydrocracking reactions to attempt to prolong its effectiveness. NiO- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> proved more effective than Ru- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst in producing the desired compounds. Fresh pre-treated catalyst proved more effective than its regenerated counterpart. Sulphur pre-treatment was found to be vital in order to

activate the catalyst for hydrocracking reactions. Higher temperatures were found to result in a greater degree of cracking and resulted in a higher yield of the target compounds. A system pressure of 120 bar was selected over the proposed 40 bar to prevent the exit lines from clogging due to waxy product formed. A larger catalyst bed with the same oil volumetric flow rate will allow for a greater residence time, thus a greater degree of cracking, and therefore a higher fraction of the target compounds in the liquid product. A small loss of liquid product was expected which resulted in a lower liquid yield being calculated. The waxy product was not analysed since it cannot be used as aviation fuel unless further processed. The gas analyser indicated trace amounts of CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>4</sub>H<sub>10</sub> gas being produced.

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