

# Novel Alcohol-Based Diesel Fuels

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## ABSTRACT

The world consumes 90 million barrels of crude oil every day. Internal combustion engines are the largest consumers of energy and are the largest source of air pollution worldwide. Diesel engines, however, consume 25-35% less fuel than conventional spark ignition engines. The opportunity now exists to combine improved diesel engine technology with a renewable, non petroleum-based, alternative diesel fuel. **JGS Research** has developed a product based on alcohols in combination with an ignition promoter that has the advantage of being renewable and environmentally friendly.

**Keywords:** diesel, ignition-promoter, ethanol, methanol

- Carbon monoxide emission is negligibly low
- Total hydrocarbon and NOX emissions are lower
- Soot-free combustion

Table 1 summarizes certain well known examples of ignition promoters. Although the feasibility of these fuels was established in small field trials (notably Avocet in Stockholm's commuter buses), the high cost and explosive nature of these additives blocked their large scale implementation. **Bionit**, however, provides a low cost alternative because it is derived from cheap feedstocks. Just as important, **Bionit's** margin of safety is significantly higher than that of other ignition promoters.

## 1 BACKGROUND

Alcohol based fuels represent the most promising alternative to petroleum. Ethanol and methanol can be produced economically in sufficient quantities to have an impact on petroleum consumption and prices. Brazil, for example, produces enough ethanol at \$1.00 a gallon to supply 20% of its vehicle market. Methanol, on the other hand, is produced from natural gas. The primary market for methanol is the chemical industry. The current annual market for methanol is 32 million tons a year. The price for a gallon of methanol in 2007 has ranged between \$1.00 and \$2.00 per gallon. If the market for methanol were to become predominantly fuel based, production could be increased 2-3 fold over the next 5 years.

The historical challenge with using ethanol and methanol alone as primary fuels is that they require significant engine modifications. The use of certain additives, termed ignition promoters, improves the ignition quality of alcohols so that they can be utilized as diesel fuels. **Bionit**, developed by **JGS Research** is such a product.

**Bionit** is a novel product, but the idea of using additives to make the use of alcohols possible for use in diesel engines started in the in the mid 1970's as a result of the dramatic rise in crude oil prices and the focus on alcohol based alternative fuels. It was shown that ethanol with an ignition promoter additive had several environmental benefits when compared with regular diesel fuel:

Ignition Promoter (IP)	Company	Major component	Based on	Required amount of IP
Kerobrisol MAR	BASF	cyclohexyl nitrate	phenol	10 %
Cetanol 105	Nitro Nobel	isopropyl nitrate	mineral oil	25 %
DII3	Ethyl Corp.	octyl nitrate	crude oil	16 %
DEGDN	Oxiteno	diethylene glycol dinitrate	ethanol	5-6%
Avocet	ICI	Poly ethylene glycol dinitrates	Proprietary	4 %
<b>BIONIT</b>	<b>JGS Research</b>	<b>Nitrated Carbo hydrates</b>	<b>Polysugar Residues</b>	<b>10-15%</b>

Table 1: Examples of Ignition Promoters

## 2 PROCESS OVERVIEW

### 2.1 Oxidative Solubilization

The first step in the production of **Bionit** is oxidative solubilization. It can be tailored to any one of a number of diverse feedstocks. The novel aspect of this process is that it achieves the depolymerization of hemicellulosic residues through acid catalysis at 1-2 atmospheres in methanolic media. This allows the separation of the reactive hemicellulosic species from cellulose. The resulting monomeric sugars (carbohydrates) have between 3-6 hydroxyl groups that provide the reactive sites in the subsequent steps. Yield is dependant on the feedstock used as well as the degree of hydration of the feedstock.

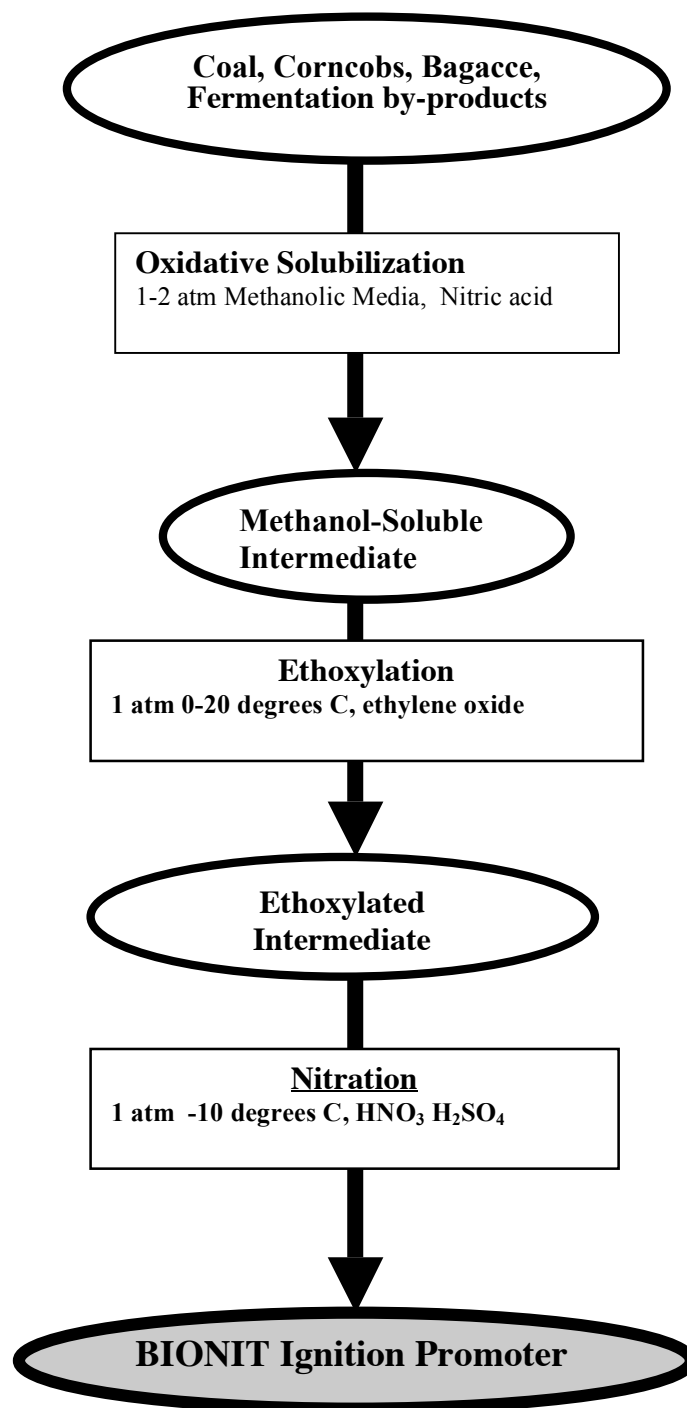
### 2.2 Ethoxylation

The second step in the production of **Bionit** is the addition of ether functionality through the reaction with oxiranes. As is illustrated in the process schematic, the chosen oxirane is ethylene oxide, which reacts stoichiometrically at minus 20 to 0 degrees centigrade. An important feature of this intermediate is that it exhibits a marked decrease in viscosity from its precursor. This is of paramount importance in its being suitable for use as a cetane enhancer (ignition promoter).

### 2.3 Nitration

The final step in the production of **Bionit** is nitration. This is accomplished in a novel fashion through the utilization of a continuous flow reactor. Compared with conventional batch nitration, this method allows partial nitration of our intermediate. We can thus choose the nitrogen content of our product in the range of 7-15%. Varying nitrogen content allows us to tailor our process to different feedstocks as well as a spectrum of product requirements. This process also has the advantage of a significantly higher margin of safety since the reaction volume is much smaller than with batch nitration. A final advantage is that this method allows us to continuously monitor product production, permitting dynamic reaction adjustments to ensure a consistent product.

## 3 PROCESS SCHEMATIC



## 4 RESULTS

**JGS Research** has experience developing ignition promoters from an array of diverse feedstocks ranging from bituminous coal, lignite, and peat to biomass-derived feedstocks such as corncobs, newspaper and bagasse. The initial research, dating to 1980, was undertaken in collaboration with and funding from The Ontario Research Foundation (currently Bodycote-Ortech), The New York State Energy Research and Development Authority (NYSERDA) as well as the US Department of Energy. More recently, JGS Research, in conjunction with the Saskatchewan Energy Authority, has conducted research on a more economical substitute for Avocet based on fermentation residues (waste) from their ethanol production.

This research has resulted in the development of a proprietary process (US Patents **4,762,529**; **4,760,803**; **4,668,243**; **6,280,487**) that allows the depolymerization and subsequent functionalization of biomass into monomers. We then effect a second functionalization and eventual nitration to obtain starting materials of suitable viscosity for the production of an ignition promoter. Ignition tests of the **Bionit** ignition promoter yielded promising results. The high degree of nitration, (11%-13% in “Bionit”) produce an ignition promoter with a favorable ignition profile.

In collaboration with the New York State Energy Authority and Daimler Benz AG it’s suitability as a diesel fuel was summarized as follows:

**“Bionit-M, a nitroester product from waste newspaper was tested as an ignition accelerator for methanol in its use as a fuel for high speed Diesel engines. At a concentration 12% by weight it was found as effective as the reference fuel with 6% of TEGDN...”**

In a subsequent collaboration with the Ontario Research Foundation (currently Bodycote-Ortech), products derived from corncobs and peat were evaluated. The Ontario Research Foundation summarized the results as follows: **“Methanol test fuels mixed with novel ignition promoters (IP) were evaluated in a single cylinder direct injection Ricardo Hydra engine. Baseline data were generated on diesel and a methanol IP mixture, commercially available... test fuels showed combustion characteristics which are acceptable, peak pressures similar to diesel, reduce rate of pressure rise despite faster combustion (reduced combustion duration)”**

Most recently, in collaboration with the Saskatchewan Energy Authority, **JGS Research** investigated the suitability of fermentation byproducts for use as feedstock for **Bionit**. The resulting product was tested by the US Environmental Protection Agency (Ann Arbor) through a subcontractor (FEV). Ignition/pressure

tracings demonstrate the ignition profiles are similar to our earlier products.

## 5 SAFETY PROFILE

Our product with a nitration degree of N=12% meets required safety tests. With the exception of autoignition, the ignition promoter was insensitive at the upper limits of the testing equipment in regards to impact, friction, and electrostatic discharge. This is in marked contrast to other ignition promoters of similar nitrogen content which require desensitizers to achieve an acceptable safety profile. (Safety profile as characterized by an independent testing laboratory, Atlantic Research Corporation see Table 2)

Auto-ignition	Impact	Friction	ESD
172 C	>300 kg-cm	>1800 psi	> 6 joules

Table 2: BIONIT Safety Profile.

## 6 COST

Because the feedstock for the production of the **Bionit** ignition promoter is a byproduct of primary fermentation, the material is readily available wherever there exists an ethanol production facility. The process itself, as outlined in the appendix utilizes temperatures in the range from 0-110 degrees centigrade. Although the initial depolymerization requires pressures in the 1-2 atm range, the entire process employs readily available reagents that allow the production of an economical product.

## 7 FUTURE

**JGS Research** has developed a proprietary process patented in the United States under patent numbers: **4,668,243**, **4,760,803**, **4,762,529**, and **6,280,487**. We have demonstrated the technical feasibility of utilizing this process for the production of ignition promoters and are interested in bringing **Bionit** to market. At this time we are considering formal collaborations and licensing opportunities.