Catalysis Letters 12 (1992) 105–116

New and improved catalytic processes for clean fuels

I.E. Maxwell and J.E. Naber

Koninklijke / Shell-Laboratorium, Amsterdam (Shell Research B.V.), Badhuisweg 3,
1031 CM Amsterdam, The Netherlands

New and more stringent environmental legislation is expected to have a major impact on the refining industry. Reformulated gasoline which is currently being introduced into parts of the United States is an example of the shift towards "cleaner" burning fuels. To achieve future government specifications for such fuels significant changes will likely be required in refinery operations to produce products with good combustion characteristics and reduced emissions.

Catalysis is expected to play a dominant role in both modifying existing processes and developing new routes to these more environmentally acceptable fuels. Both new and improved catalysts systems which will be required for the production of so-called reformulated gasoline are discussed. For example, oxygenated components in gasoline such as methyl tertiary butyl ether (MTBE) will continue to be required on a large scale necessitating new process and catalyst technology to achieve improved economics.

Natural gas can be considered as a "clean" feedstock from which to produce liquid fuels of high quality. A number of new process routes to convert remote natural gas into readily transportable liquid fuels are also discussed. This area of technology offers considerable scope for further major improvements based on innovation in the field of syngas catalysis.

Keywords: Catalysis; clean fuels; reformulated gasoline; ethers; oil refining; natural gas conversion

1. Introduction

The trend towards increasing environmental awareness and the consequent tightening of governmental legislation is having a major impact on the process industry of which the oil refining business is a significant component. This paper is intended to highlight some of these trends and the expected technological response in which catalysis will play a key role.

In the past 10–15 years there has been a significant drive to maximize the upgrading from a barrel of crude oil which has led to increased residue conversion. Both catalytic (e.g. long residue catalytic cracking) and non-catalytic (e.g. flexicoking) processes have been successfully developed and applied to convert heavy oil fractions into lighter more valuable transportation fuels (i.e. gasoline, kerosine and gasoil).

In addition to the economic incentive to upgrade the "bottom of the barrel", environmental forces will also dictate processing of residue containing feedstocks. Parallel to the residue conversion developments in recent years interest has grown to also upgrade the "top of the barrel" (i.e. C_1–C_4 components). In contrast to residue conversion where thermal and catalytic cracking processes are applied to reduce molecular weight for light ends upgrading "synthetic" products with increased average molecular weight are required employing catalytic processes such as oligomerization or paraffin alkylation. It is expected from both economic and environmental considerations that the trends towards increased upgrading of both the "top and bottom" of the barrel will continue in the future.

Product quality has also gained in emphasis in recent years which has focussed attention towards processes that upgrade in terms of product performance aspects rather than simply a change in average molecular weight. Both environmental legislation and product differentiation in the market place will continue to stimulate this trend in the oil refining industry.

Studies related to both toxicity and the atmospheric reactivity of gasoline components have led to governmental guidelines for "cleaner" or so-called reformulated gasolines. These factors include: reduced volatility of hydrocarbons (e.g. butane); lower levels of benzene; reduced heavy aromatics; reduced photochemically reactive hydrocarbons and the introduction of oxygenates such as alcohols and ethers.

An important on-going study in this regard is the Auto/Oil Air Quality Improvement Research Programme (AQIRP) which is directed towards understanding in detail the effects of fuel property changes on vehicle emissions.

Oxygenated components have found favour in these reformulated gasolines which have already been introduced into the market place in parts of the US in anticipation of pending legislation. These oxygenates have been shown to reduce engine tail pipe emissions with respect to both carbon monoxide and unburned hydrocarbons. Tail pipe emissions are reduced by adding oxygenated components to the gasoline fuel mixture up to a level of about 3.0% wt. oxygen. In addition to the positive environmental effect oxygenates and, in particular, ethers have very attractive octane properties with regard to both research octane

Table 1
Some gasoline components

	RON	MON	Volatility (RVP) (psi)
MTBE	118	100	8–10
ETBE	118	102	3–5
TAME	111	98	1.5
i C_5/C_6	75–102	75–102	6–27
Alkylate	92–97	90–94	3.5–4.5

(RON) and motor octane (MON) numbers as shown in table 1. This combined octane and reduced emissions benefit has contributed to the rapid growth in the use of ethers, particularly methyl tertiary butyl ether (MTBE), in recent years despite the uncertainties that existed with regard to environmental legislation.

2. Catalytic processes to "clean fuels"

2.1. ROUTES TO MTBE

MTBE is readily manufactured from iso-butene and methanol by an acid catalysed etherification process. Higher ether anologues can also be manufactured as shown in fig. 1 by making use of a higher alcohol or a higher iso-olefin resulting in, for example, ethyl tertiary butyl ether (ETBE) and tertiary amyl ether (TAME). To date, ETBE and and TAME have not found wide application due to the relatively high cost of ethanol compared to methanol and the limited availability of iso-pentene relative to iso-butene, respectively. However, the higher ethers offer volatility advantages compared to MTBE and more cost effective routes to these molecules would be advantageous although it does become more difficult to catalyze the etherification reactions for the higher ethers. Using conventional ion-exchange resin catalyst systems, both the reaction temperature requirement increases and the yield of product decreases as the feed carbon number increases from C_4 to C_8. This limitation poses a challenge to develop improved ion-exchange resin catalysts for the production of higher ethers.

The projected growth in MTBE is expected to result in a short supply of iso-butene which is currently produced as a by-product of steam cracking and catalytic cracking processes. This anticipated shortage has resulted in studies of either modified or alternative process routes to iso-butene. For example, a catalytic cracker product yield structure can be modified [1] by the addition of

ETHER BUILDING BLOCKS

- (Lower) iso-olefins
- Lower alcohols

Isobutene + Methanol ⟶ MTBE
Isobutene + Ethanol ⟶ ETBE
Isopentene + Methanol ⟶ TAME

Limiting factor: iso-olefin availability

Fig. 1. Routes to typical gasoline ether components.

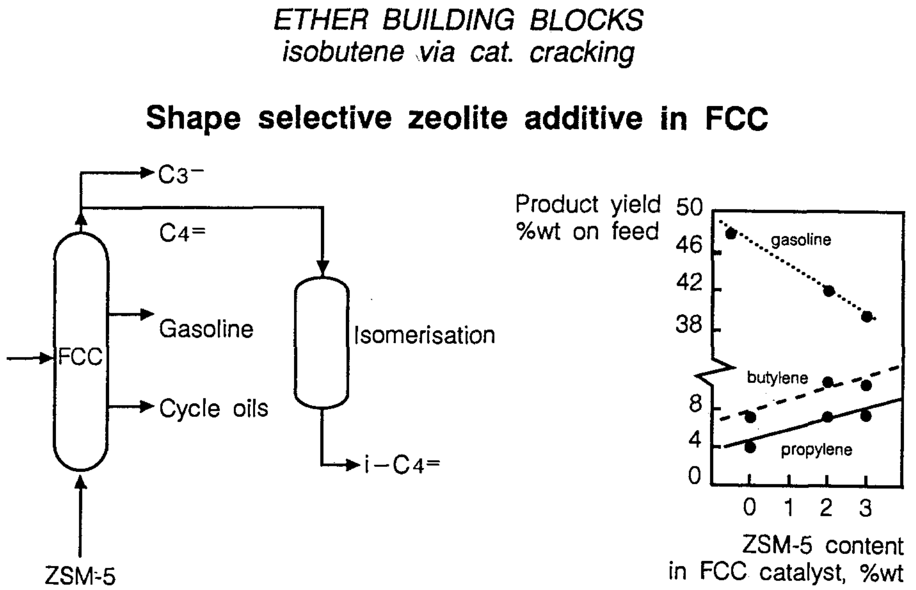

Fig. 2. Iso-butene manufacture using a ZSM-5 zeolite additive in fluid catalytic cracking (FCC).

an additive catalyst in the form of a medium pore zeolite (e.g. ZSM-5). As shown in fig. 2, this results in a significant increase in C_3 and C_4 olefins which can substantially increase the production of iso-butene via catalytic cracking.

This increased olefins make does, however, occur at the expense of gasoline yield but it is expected that the olefins values should compensate for this loss and the addition of the MTBE product to the gasoline pool will both reduce aromatics and improve octane quality.

Alternative routes to iso-olefins involve the combination of isomerization and dehydrogenation of paraffins. The Butamer isomerization and Oleflex dehydrogenation are existing commercial processes [2]. Paraffin dehydrogenation is the most expensive process which operates at high temperatures, is highly endothermic and involves a substantial recycle stream due to limited conversion per pass resulting from thermodynamic limitations.

2.2. PARAFFIN ISOMERIZATION

Paraffin isomerization is an attractive process route to produce both high octane and environmentally acceptable gasoline components. The research octane numbers of C_5 and C_6 iso-paraffinic molecules are significantly higher than their normal anologues which results in a substantial increase in RON. This skeletal isomerization is, however, an equilibrium limited reaction whereby low temperatures favour high conversion and thus high octane products. Very low temperatures of some 150°C can be employed by using chlorided alumina type catalysts containing a noble metal such as platinum which is employed in

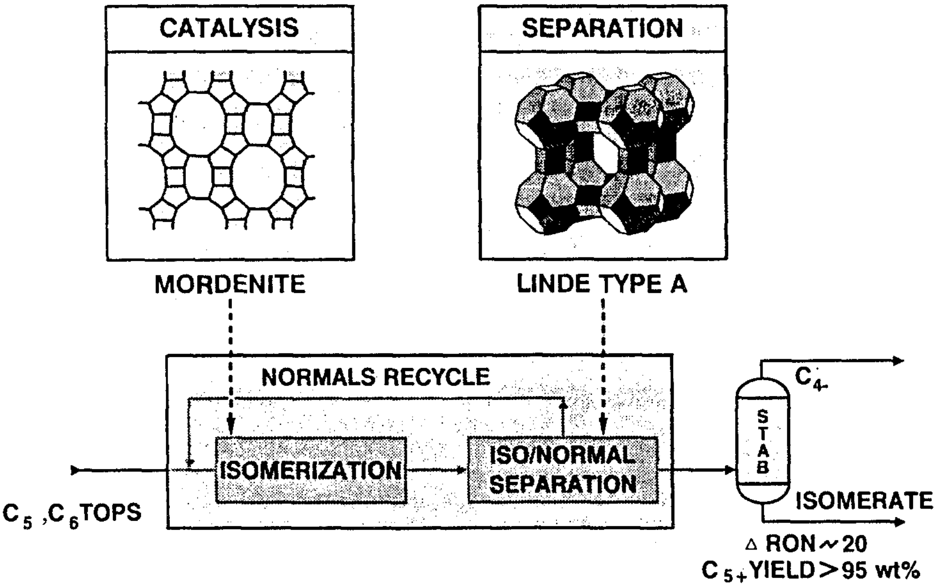

Fig. 3. The Shell/UOP paraffin total isomerization process (TIP).

the UOP PENEX process. However, these catalyst systems are quite sensitive to trace impurities in the feed such as water. By contrast, zeolite based catalysts which operate at somewhat higher temperatures (i.e. 250°C) are more robust and can withstand low levels of impurities such as sulphur and water in the feedstock. Such catalysts were first developed for the Shell Hysomer process [3] using platinum/mordenite as the zeolite component. At these temperatures the equilibrium is such that some normal paraffins are not fully converted to branched products and it can therefore be attractive to combine Hysomer isomerization with the ISOSIV-iso/normal separation process was developed by Union Carbide, now owned by UOP.

In the ISOSIV process the normal paraffins are selectively adsorbed by zeolite 5A, while the branched isomers cannot enter the small pores of the molecular sieve. The effluent of the Hysomer process can thus be separated in the ISOSIV step and the normals recycled back to the catalytic section whereby complete conversion to iso-paraffins is achieved. This is the basis of the joint Shell/UOP process, known as TIP (Total Isomerization Process) as shown in fig. 3, which results in an increase of some 9–10 octane (RON-O) points compared to the single-step Hysomer process [4].

It would, however, be advantageous to be able to extend paraffin isomerization beyond C_5/C_6 paraffins and thereby increase the volume of isomerate which could be produced in the refinery. This cannot currently, however, readily be achieved as was demonstrated in studies by Weitkamp [5]. He published results on the hydrocracking and hydroisomerization over a bifunctional zeolite

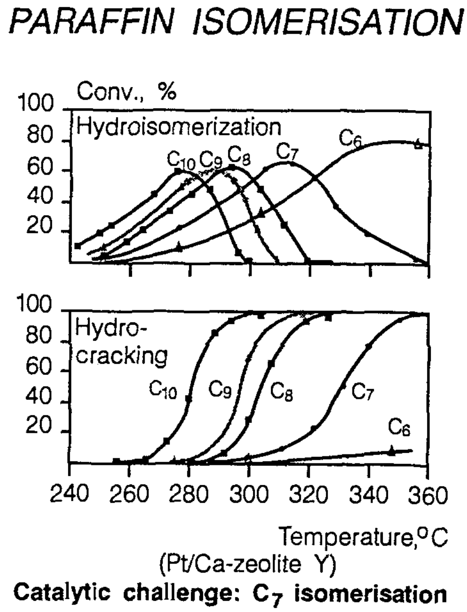

Fig. 4. Hydroisomerization and hydrocracking of n-paraffins as a function of temperature (from ref. [5]).

catalyst for alkanes of various chain lengths as shown in fig. 4. The following general trends can be discerned, namely: higher molecular weight alkanes are much more reactive than their lower analogues and isomerization proceeds at lower temperatures than hydrocracking. Thus, a feedstock with a wide boiling point range will result in cracking of the heavier components and only isomerization of the lighter molecules. In addition, to achieve a significant octane upgrading for the higher molecular weight paraffins a relatively high degree of branching per molecule is required. This high degree of branching is difficult to achieve without significant selectivity losses due to cracking reactions.

Although paraffin isomerization is already being quite extensively applied a second wave of growth could likely occur as refiners seek to reduce aromatics in reformulated gasoline.

2.3. PARAFFIN ALKYLATION

Paraffin alkylation is a process which involves the alkylation of i-butane with propene and/or butenes to produce highly branched C_7, C_8 paraffin products with attractive high octane properties. In particular, the relatively high motor octane (MON) rating of alkylate means that this process is often applied to meet the overall gasoline pool MON specifications.

However, the alkylation process suffers from a major disadvantage in that specific acidic catalysts are required to catalyse the reactions involved. Further-more, the only acids which can currently be applied are H_2SO_4 and HF in the liquid phase which impose significant safety and environmental constraints on the processes. In the case of H_2SO_4 a large amount of the acid is consumed during the process which needs to be regenerated on-site and the safety concerns related to HF limit the size of the acid storage facilities and thus restrict the process capacity. Both these factors serve to severely constrain the growth in the alkylation process despite the very attractive product properties also from an environmental view point.

The development of a heterogeneous catalyst system based on a solid acid with the correct surface properties could potentially remove the existing constraints and lead to wider and larger scale application of paraffin alkylation as an environmentally attractive high octane gasoline producing process.

2.4. GAS CONVERSION PROCESSES

The evolution of proven world oil and gas reserves exhibits a dramatic increase in the latter and a leveling off of the former. This trend is expected to continue, which will result in a shift towards the use of gas as a feedstock for the large scale manufacture of transportation fuels and even petrochemicals. Recognition of this situation has led to increased global interest in new emerging technologies which can efficiently convert natural gas into liquids and higher added-value-products. The incentive to produce ambient temperature liquids from gas also stems from the desire to employ such process technology directly at remote natural gas field sites and thereby save on expensive gas transportation costs. This new process technology could thus potentially compete favourably with, for example, liquified natural gas (LNG) tankers which are the present prime means of gas transportation to consumers from remote gas fields. In addition, natural gas has some attractive features as a feedstock in that it can be readily purified on-site to provide a very clean and hydrogen rich source of hydrocarbon. The lack of heteroatoms, metals and aromatic structures in such a feed can be most advantageous as the world demand for clean fuel products increases.

A number of natural gas conversion processes are already commercial or at an advanced stage of development, some examples of which are shown in fig. 5. Most of these process technologies involve the initial conversion of methane into syngas (CO/H_2) followed by further processing to obtain the desired liquid product. Since the syngas manufacturing step is expensive there has been considerable research into alternative so-called direct routes in which this costly step is avoided. One of the most promising direct conversion routes is based on catalytic oxidative coupling of methane (see fig. 5). Arco has been one of the most prominant companies working in this field having progressed to the pilot plant phase [6]. The primary products are ethane and ethylene but the yields obtained to date are not sufficiently high to warrant commercialization.

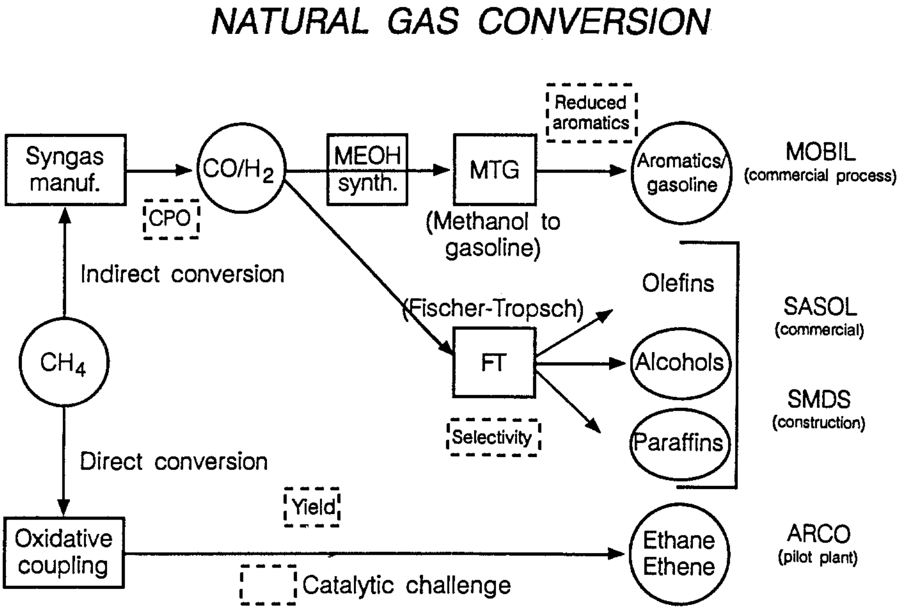

Fig. 5. Some developmental and commercial catalytic natural gas conversion processes.

The indirect routes via syngas have progressed further in terms of commercial development. Process technology based on Fischer-Tropsch catalysis was successfully developed in Germany during the second World War using coal as the source of hydrocarbon feedstock. This technology was further developed and applied on a large commercial scale in South Africa by the Sasol company also using coal as the feed. The Fischer-Tropsch route can potentially produce a variety of products including olefins, alcohols and paraffins. The product mix obtained can be controlled to some degree depending on the catalyst system used. The existing Sasol process makes use of an iron based F-T catalyst which is inexpensive and also produces the full spectrum of products.

More recently Shell [7,8] has developed the so-called Shell Middle Distillate Synthesis process (SMDS) which uses natural gas as the feedstock and therefore results in a more hydrogen rich syngas than is produced from coal. The SMDS process was primarily designed to produce a high quality diesel/gasoil as the major product. Since F-T catalysis involves a chain growth mechanism which obeys Schultz-Flory kinetics this poses a problem in designing such a process to produce a narrow carbon number range product. This has been achieved in the SMDS process by applying two steps involving a first step in which a high molecular weight paraffinic product (wax) is produced by F-T catalysis and a second step in which the wax is selectively hydrocracked back to a middle distillate boiling point range product (see fig. 6). An essential feature of the F-T step is to use a proprietory catalyst which will selectively produce wax (so-called

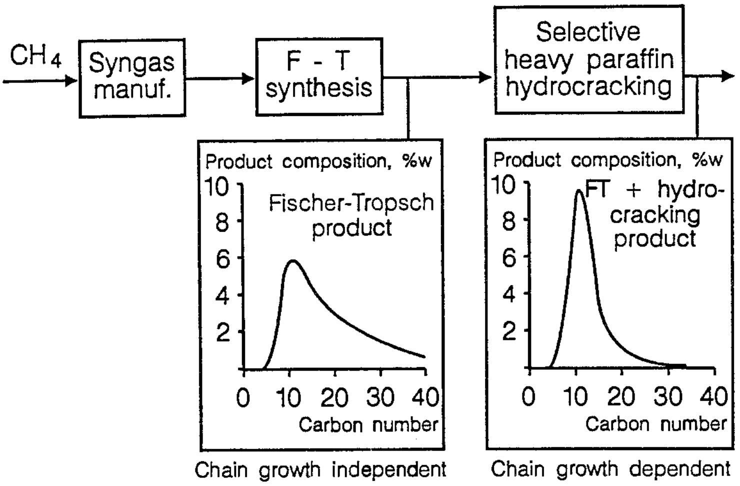

Fig. 6. A schematic of the Shell Middle Distillate Synthesis (SMDS) process showing the final and intermediate product compositions as a function of carbon number.

high alpha-value). Promoters are also used to improve catalyst selectivity and activity.

It has been announced that the first commercial SMDS plant will be constructed in Malaysia making use of a remote natural gas field to provide the methane feedstock. A synthetic gasoil product of very high quality (cetane number) is produced by this process which also contains no heteroatoms or aromatic structures. This SMDS produced gasoil has further environmental advantages whereby a reduction in particulate emissions may be realized during combustion compared to a gasoil obtained from a conventional refinery.

Another important natural gas conversion process is the Mobil developed (fig. 5) methanol-to-gasoline (MTG) process [9]. This process was developed in the seventies and early eighties at the peak of the energy crisis and high oil prices. The unique feature of this process is the selective conversion of methanol using a shape selective zeolite (ZSM-5) to yield an aromatic product which boils in the gasoline range. Methanol is produced from syngas using conventional technology and the syngas is made by steam reforming of natural gas. In practice the MTG reaction is carried out in two steps whereby dimethylether is produced as an intermediate product.

The first commercial unit based on this technology is successfully operating in New Zealand utilizing offshore natural gas reserves and thereby significantly reducing the countries dependence on imported crude oil. In the meantime Mobil have developed a more advanced process design which utilizes fluid bed rather than fixed bed reactors for improved product selectivity and heat removal. Other companies have developed multifunctional catalyst systems which obviate the need to isolate methanol as an intermediate product.

The relatively low oil prices in recent years have, however, adversely affected the economics of natural gas conversion processes, particularly when the primary products only command conventional liquid fuel prices in the market place. Nevertheless, as world oil reserves are further depleted in the future, alternative natural gas based technologies will likely increase in importance particularly for higher value added products such as chemicals.

3. Conclusions and future challenges

It should be evident from the foregoing discussion that catalysis will play a vital role as the oil refining industry responds to the challenges of producing "cleaner" fuels and higher quality oil products. This will require both improved catalysts for existing processes as well as novel catalyst systems for new processes.

As regards new processes the discovery of a viable heterogeneous paraffin alkylation catalyst would represent a major breakthrough and in all likelihood such a process would be applied on a much larger scale than is currently practiced due to the reduced safety risk and the attractive product properties as components for reformulated gasoline. The rapidly growing demand for components such as MTBE will lead to construction of world scale butane dehydrogenation plants. This technology is currently relatively expensive and would greatly benefit from both improved catalysts and process technology. New inexpensive catalytic routes to alternative ether components other than MTBE would be advantageous particularly if crude olefinic refinery streams could be used as feedstock.

Natural gas conversion also offers significant challenges in the field of catalysis and is expected to grow in importance to both exploit remote natural gas fields and produce environmentally attractive fuel products.

In summary, innovation in catalytic technology will be vital to the refining industry as it adapts to the rapidly changing demands of new "clean fuels" directed environmental legislation and market driven improved product quality.

References

[1] J. Biswas and I.E. Maxwell, Appl. Catal. 58 (1990) 1–18.
[2] R.C. Berg, B.V. Vora and J.R. Mowry, Oil & Gas J., Nov. 10 (1980) 191–197.
[3] H.W. Kouwenhoven, *Molecular Sieves*, ACS, Advances in Chemistry Series 121 (1973) 529–539.
[4] I.E. Maxwell, Zeolites in hydroprocessing technology, Catal. Today 1 (1987) 385–413.
[5] J. Weitkamp, *Hydrocracking and Hydrotreating*, ed. J.W. Ward, ACS Symposium Series 20 (American Chemical Society, 1975) 1–27.
[6] C.A. Jones, J.J. Leonard and J.A. Sofranko, Energy & Fuels 1 (1987) 12–16.

[7] J. Eilers, S.A. Posthuma and S.T. Sie, The Shell Middle Distillate Process (SMDS), AIChE Spring National Meeting, Orlando, Florida, USA, 18–22 March (1990).
[8] M.J. van den Burgt, C.J. van Leeuwen, J.J. Dell'Amico and S.T. Sie, The Shell Middle Distillate Synthesis Process, in: *Methane Conversion*, eds. D.M. Bibby, C.D. Chang, R.F. Howe and S. Yurchak (Elsevier Science Publishers B.V., Amsterdam, 1988) 473–482.
[9] C.D. Chang and A.J. Silvestri, ChemTech (October 1978) 624–631.