

# Low-pressure Methanol/ Dimethylether Synthesis from Syngas on Gold-based Catalysts

**Arthur Mpela<sup>1,\*</sup>, Diane Hildebrandt<sup>1</sup>,  
David Glasser<sup>1</sup>, Mike S Scurrall<sup>2</sup>,  
Graham J Hutchings<sup>3</sup>**

<sup>1</sup> School of Chemical and Metallurgical Engineering,  
University of the Witwatersrand, Johannesburg,  
Private Bag 3, PO Wits 2050, South Africa

<sup>2</sup> Molecular Sciences Institute, School of Chemistry,  
University of the Witwatersrand, Johannesburg,  
Private Bag 3, Wits 2050, South Africa

<sup>3</sup> School of Chemistry, Cardiff University, PO Box 912,  
Cardiff, CF19 3TB, UK  
E-mail: scurrall@chem.wits.ac.za

## Abstract

**The hydrogenation of carbon monoxide over Au/ZnO catalysts has been re-examined and new data is presented on the way in which the product distribution can be manipulated by choice of co-added solids such as alumina or zeolite-Y. This comparative study reveals that while ZnO itself leads to a high selectivity to methanol, the incorporation of gold drastically alters the product spectrum and leads to a very high selectivity to hydrocarbons. The hydrocarbon selectivity at a reaction temperature of 300°C is in fact much higher than in the case where alumina or zeolite-Y is introduced into a composite catalyst comprising the Au/ZnO and the acidic solid. In the latter case DME is a major product. Significant light hydrocarbon formation on gold-based systems under these circumstances appears not to have been discussed before. The reactions taking place on these catalysts, the selectivities and absolute activities are discussed and the role of gold highlighted.**

## Introduction

The current technology used for methanol synthesis requires high pressure (>120 atm) to reach an acceptable CO conversion. However, the transformation of methanol into DME (dimethylether) can be used to relieve the thermodynamic constraints for high operating pressure, and methanol/DME mixtures may be a more desirable product in some circumstances. If the methanol and DME synthesis take place in the same reactor at the same conditions, one should in principle be able to use a much lower operating pressure, making a potentially cheaper large scale process to produce methanol and DME which are proposed as the preferred alternative clean fuels for diesel engines (1, 2).

The catalysts that are needed for this co-production have to be stable, selective and actively able to catalyse the main reactions (methanol and DME synthesis) involved in this process at the same temperature. Unfortunately existing commercial copper-based methanol catalysts are not able to function efficiently in the presence of large concentrations of water or at high temperature (3). PGM (Platinum Group Metals)-based catalysts usually suffer from the methanol selectivity decreasing when the operating temperature increases. Moreover, the PGM materials are relatively expensive and their market prices are relatively unstable (4). Therefore, it remains of interest to develop a more satisfactory and competitive catalyst for methanol/dimethylether synthesis.

Catalytic studies done on metallic gold have shown that supported gold nano-particles can be used as catalyst for the hydrogenation of carbon oxides (5, 6). Accordingly, this study investigates the possibility of using bifunctional based gold catalysts for the methanol and dimethylether co-production at relatively low pressure.

## Experimental

### Catalyst preparation

The catalysts used in this study were: ZnO, 5%Au/ZnO, 5%Au/ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 5%Au/ZnO/LZ-Y52 that were prepared as follows:

The 5%Au/ZnO samples were synthesised by a co-precipitation method using dilute solutions of H<sub>2</sub>AuCl<sub>4</sub>·xH<sub>2</sub>O (Next Chimica) and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Aldrich) and a solution of Na<sub>2</sub>CO<sub>3</sub>. An aqueous solution of tetrachloroauric acid and zinc nitrate was introduced dropwise into the carbonate solution under vigorous stirring for 90-120 min. The precipitation temperature was maintained at 70-80°C.

The co-precipitated sample was aged for 24 h, filtered, washed several times with warm distilled water, and then dried in the oven. The powder obtained was calcined at 400°C in air. ZnO catalyst was prepared in a similar way, but without adding the gold source. 5%Au/ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was made from a physical mixture 1:1 (mass) of 5%Au/ZnO with gamma-alumina and 5%Au/ZnO/LZ-Y52 catalyst from the physical mixture 1:1 (mass) of 5%Au/ZnO with Y-zeolite.

## Catalyst characterization

After preparation catalysts were characterised by powder X-ray diffraction using an Enraf Nonius PSD120 diffractometer with a monochromatic  $\text{CuK}_{\alpha 1}$  source operated at 40 keV and 30 mA. Phases were identified by matching experimental patterns to the JCPDS powder diffraction standard. The surface areas were determined by BET from the nitrogen adsorption isotherm, using Micrometrics Gemini equipment. Raman spectroscopy characterisation was made using a Renishaw spectrometer. The particle sizes were determined using the transmission electron microscope. ICP-AES was used to quantify impurities in catalyst samples.

## Catalyst testing procedure

The catalysts used in this study were tested in a stainless steel tubular reactor with an external diameter of  $\frac{1}{4}$  inch. For ZnO and 5%Au/ZnO, only 0.3 g was used, whereas 0.6 g was considered in the case of 5%Au/ZnO/ $\gamma\text{-Al}_2\text{O}_3$  and 5%Au/ZnO/LZ-Y52 in the ratio 1:1. The catalyst was pre-treated with pure hydrogen under atmospheric pressure at 250°C for 2 h with a gas flow rate of 10 (stp)mL/min. After reduction, the gas was changed for syngas ( $\text{H}_2/\text{CO}/\text{N}_2 = 60/30/10$ , Afrox) and the reactions conditions (10 mL(stp)/min, 300-400°C, 2.5 MPa) were adjusted. In the operating conditions of this work the steady state was achieved after 4 hours of reaction. Gas chromatography (a Varian GC 4290 unit) was used to analyse the inlet and exit streams; CO,  $\text{H}_2$ ,  $\text{N}_2$  (as internal standard)  $\text{CO}_2$  and methanol were determined using a 1.5m  $\frac{1}{8}$  inch diameter Carboxon packed column with TCD detection, and, simultaneously methanol and all other oxygenates and hydrocarbons were determined using a Porapak-Q column (also 1.5 m length,  $\frac{1}{8}$  inch diameter) with FID detection. The columns were used in a temperature programmed oven, with initial and final temperatures of about 50 and 200°C respectively, with a ramping rate of 10°C/min and a final hold period of 40 min at 200°C.

## Results and discussion

It can be seen in Figure 1, the XRD pattern presents only the diffraction lines of the support ZnO. The gold particles are too small at the loadings used to give rise to well-defined lines.

Raman spectroscopy analysis was associated revealed new bands observed at 3230 and 3483  $\text{cm}^{-1}$  for 5%Au/ZnO due to hydroxyl groups associated at the interface of nanogold and ZnO (Figure 2).

Transmission electron microscopy images (see Figure 3) were used to determine a mean gold particle size in the samples of close to 6nm.

The specific surface area of 5%Au/ZnO sample as determined from BET was 49  $\text{m}^2/\text{g}$ .

Amongst all hydrocarbon products, methanol was formed with high selectivity (Table 1) accompanied with some traces of hydrocarbons when ZnO was tested at 300°C and 2.5MPa.

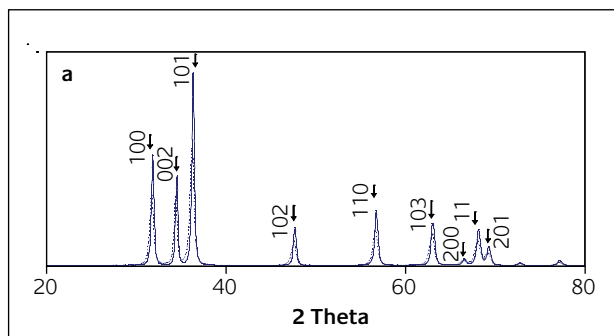


Figure 1

XRD diagram of 5%Au/ZnO catalyst and ZnO support

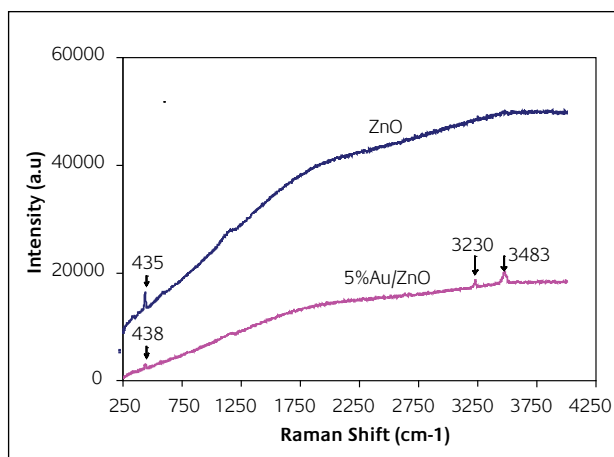


Figure 2

Raman spectra of ZnO and 5%Au-ZnO catalysts

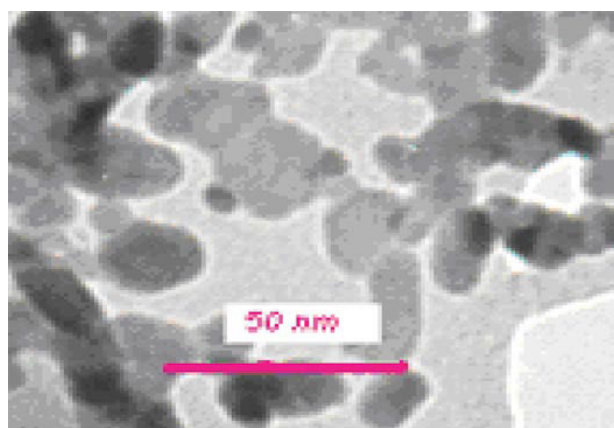


Figure 3

TEM micrograph of 5%Au/ZnO

The specific rate of formation of methanol (on ZnO) was 129  $\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$  and the total CO conversion was 1.2%. The production of hydrocarbons was markedly higher in the case of the gold-containing catalyst and may reflect a tendency for Fischer-Tropsch activity to develop in the gold-based catalyst. An alternative source of hydrocarbons is the methanol and/or DME. The typical transformation of methanol into hydrocarbons is well known (7-9), and though this process is normally associated with the action of acid catalysis (7-9), other mechanisms have been proposed

**Table 1**

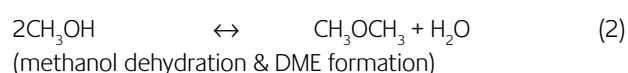
Hydrocarbon products distribution (mass %) over gold-based catalysts at 300°C

Product	Catalyst				
	ZnO	5%Au/ZnO	5%Au/ZnO/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	5%Au/ZnO/LZ-Y52	Blank reactor
CH <sub>4</sub>	1.17	28.1	21.5	17.6	nd
C <sub>2</sub> H <sub>4</sub>	0.667	3.17	4.13	19.7	nd
C <sub>2</sub> H <sub>6</sub>	0.174	10.1	13.7	6.38	nd
C <sub>3</sub> H <sub>6</sub>	0.555	9.63	5.87	12.8	nd
C <sub>3</sub> H <sub>8</sub>	nd	4.65	6.40	nd	nd
CH <sub>3</sub> OCH <sub>3</sub>	nd	nd	33.1	20.1	nd
CH <sub>3</sub> OH	96.8	4.21	nd	nd	nd
C <sub>2</sub> H <sub>5</sub> OH	nd	nd	nd	16.2	nd
C <sub>4</sub> H <sub>8</sub>	0.289	4.92	1.52	6.67	nd
C <sub>4</sub> H <sub>10</sub>	0.385	8.66	6.50	nd	nd
C <sub>5</sub> H <sub>10</sub>	nd	3.36	3.80	nd	nd
C <sub>5</sub> H <sub>12</sub>	nd	6.08	1.38	nd	nd
C <sub>6</sub>	nd	6.94	nd	nd	nd
C <sub>7</sub>	nd	5.56	nd	nd	nd
C <sub>8</sub>	nd	3.83	nd	nd	nd

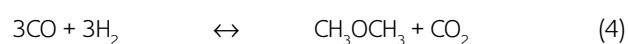
nd = not detected

to account for hydrocarbon formation over composite catalysts comprising a methanol synthesis component and a zeolitic structure (10-13). Significant acidity would not be expected to be exhibited by Au/ZnO and so further work is required in order to establish how the hydrocarbons are produced. (Blank runs with an empty reactor confirmed that no conversion of the synthesis gas took place under our reaction conditions). The formation of hydrocarbons in the presence of gold on zinc oxide is consistent with other work we have recently reported on gold-containing Fe/zinc oxide catalysts (14). We can also meanwhile note that the hydrocarbon distributions obtained by us in this work differs somewhat from those reported for Cu-Zn/zeolite hybrid catalysts such as those recently described by Asami et al (10) in that the latter observe high selectivities to C<sub>3</sub> and C<sub>4</sub> hydrocarbons, with relatively little methane, C<sub>2</sub> or C<sub>5</sub> products. In contrast, we observe significant formation of methane and C<sub>2</sub> hydrocarbons. The specific net rate of formation of methanol; on Au/ZnO was 9.8  $\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$  and that of methane was 172  $\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$  with a CO conversion level of 5.0%. The reduction (by a factor of 13) in the observed rate of formation of methanol in the presence of gold suggests that methanol producing sites are eliminated by gold or that methanol transformation to hydrocarbons is accelerated by this metal, resulting in a lower net production of the alcohol. Although methanol decomposition on gold surfaces has not yet been extensively described, there is clear evidence that decomposition to methane and carbon dioxide is not unexpected (15).

The incorporation of  $\gamma$ -alumina that acts as dehydrating agent did not greatly affect the relative distribution of hydrocarbon products, (but see below), but the new product, dimethylether, was formed and associated with an increase in CO conversion as shown in Figure 4. The observed CO conversion level was now 8.1%. This results from the dehydration (reaction (2)) of methanol formed from reaction (1) in parallel with WGSR that takes place. The reactions lead to the direct synthesis of DME from syngas (reaction (4)), albeit with a significant co-production of hydrocarbons. The relatively slight changes seen in the hydrocarbon distribution are in line with the expected catalytic action of alumina, acting largely as an acid catalyst, with slight decreases in propene and the butanes suggestive of some degree of further conversion of these alkenes, probably by oligomerization.



Overall reaction:



**Table 2**

Hydrocarbon products distribution (mass %) over gold-based catalysts at 400°C

Product	Catalyst				
	ZnO	5%Au/ZnO	5%Au/ZnO/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	5%Au/ZnO/LZ-Y52	Blank reactor
CH <sub>4</sub>	5.44	22.8	41.6	17.2	nd
C <sub>2</sub> H <sub>4</sub>	2.09	2.11	8.42	6.27	nd
C <sub>2</sub> H <sub>6</sub>	0.445	0.895	6.69	1.61	nd
C <sub>3</sub> H <sub>6</sub>	1.50	0.689	8.29	4.02	nd
C <sub>3</sub> H <sub>8</sub>	nd	nd	2.37	0.39	nd
<b>CH<sub>3</sub>OCH<sub>3</sub></b>	<b>nd</b>	<b>nd</b>	<b>15.1</b>	<b>62.4</b>	nd
<b>CH<sub>3</sub>OH</b>	<b>89.4</b>	<b>73.5</b>	<b>1.15</b>	<b>nd</b>	nd
C <sub>2</sub> H <sub>5</sub> OH	nd	nd	nd	4.06	nd
C <sub>4</sub> H <sub>8</sub>	0.803	nd	3.30	1.36	nd
C <sub>4</sub> H <sub>10</sub>	0.378	nd	3.53	1.60	nd
C <sub>5</sub> H <sub>10</sub>	nd	nd	1.46	0.92	nd
C <sub>5</sub> H <sub>12</sub>	nd	nd	2.27	0	nd

nd = not detected

The substitution for  $\gamma$ -alumina by zeolite-Y increased alkene formation, mainly ethylene and propylene, and the formation of DME (and water) increased the CO conversion significantly when compared with the CO conversions observed with 5%Au/ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 5%Au/ZnO. The CO conversion level was now 9.4%.

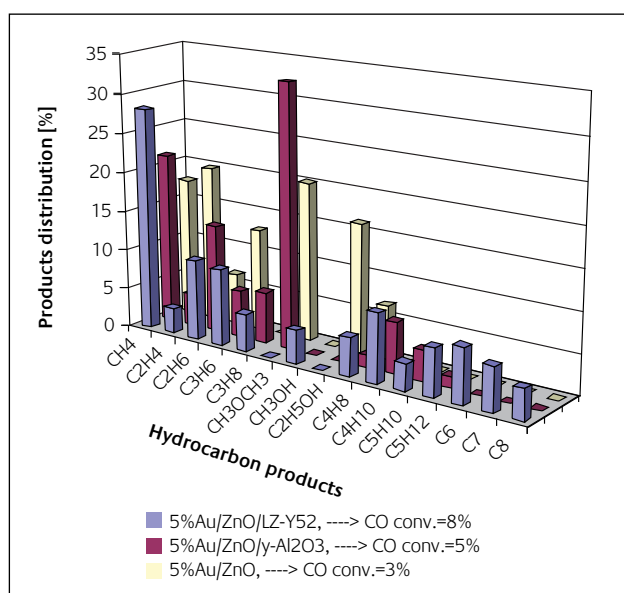
Both 5%Au/ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 5%Au/ZnO/LZ-Y52 exhibited a higher tendency for hydrocarbon formation compared with Au/ZnO (Table 2) but dimethylether is the main product for the bifunctional gold/ZnO-zeolite system.

The formation of DME over both composite catalysts increased the CO conversion (Figure 5) respectively by 60%

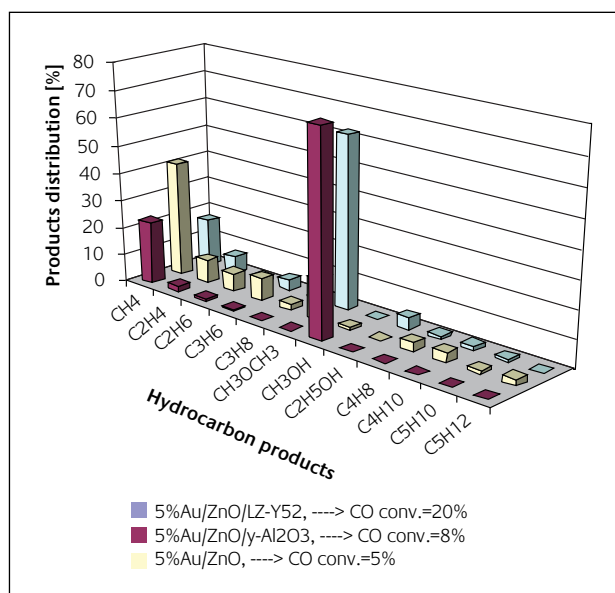
(over 5%Au/ZnO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) and 300% (over 5% Au/ZnO/LZ-Y52). (The specific rates of formation are discussed below).

Table 3 displays the selectivity and production rates obtained over bifunctional catalysts tested at 2.5 MPa and 400°C. As can be seen, the 5% Au/ZnO/LZ-Y52 catalyst yields dimethylether with relatively high selectivity and production rate. This could be related to the acidity of zeolite-dehydrating agent, as the determining rate of direct DME depends on the acid properties of dehydrating catalyst (16).

Compared with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, LZ-Y52 is more acidic, and the higher DME rate observed is a reasonable finding.



**Figure 4**  
Hydrocarbon products distribution-CO conversion over gold-based catalysts tested at 300°C, 2.5 MPa



**Figure 5**  
Hydrocarbon products distribution-CO conversion over gold-based catalysts tested at 400°C, 2.5 MPa

**Table 3**

Selectivity and production rate of selected hydrocarbon products for catalysts tested at 400°C

Selected Products → Catalyst ↓	Catalyst							
	CH <sub>3</sub> OH		CH <sub>3</sub> OCH <sub>3</sub>		CH <sub>4</sub>		CO <sub>2</sub>	
	Selectivity (%)	Production Rate (μmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> )	Select. (%)	Production Rate (μmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> )	Select. (%)	Production Rate (μmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> )	Select. (%)	Production Rate (μmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> )
5%Au/ZnO /γ-Al <sub>2</sub> O <sub>3</sub>	13.0	35.0	1.05	5.12	34.6	210	4.5	20.35
5%Au/ZnO /LZ-Y52	-	-	56.4	277.2	14.4	108	8.2	48.52

The data discussed here reflect the characteristics of the different catalysts studied. It cannot be considered a definitive study of intrinsic kinetics, and we have not yet attempted to compare product distributions on an isoconversion basis. Nevertheless, the work clearly demonstrates what may be achieved with gold-based catalysts. While the co-production of light hydrocarbons in general with DME may be considered acceptable from the viewpoint that these products could be considered as being compatible with the transportation of DME using LPG-facilities (17), the production of methane and C<sub>2</sub> hydrocarbons is generally less welcome. Future studies will focus on whether these specific products can be reduced.

Finally, we are naturally led to consider whether the gold-based catalysts having the attractive feature of enabling syngas conversion under conditions where water is a co-product, display activities comparable with those found for copper-based systems, now used for the past 35 years or so for the commercial synthesis of methanol. Direct comparison of the two catalyst systems is not entirely straightforward since the desired products (and therefore operating conditions) are not identical, but a rough assessment can be made. The total specific rate of conversion of CO on the Au/ZnO system, for example, at 573K is 840 μmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>. For copper-based catalysts of the Cu-Zn-Al type under our experimental conditions of temperature and pressure, the rate is expected to be in the range 1200 - 3600 μmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> (18, 19). Given that we have, not yet attempted to optimize the gold catalyst composition or the catalyst synthesis procedures, the activities of the gold-containing systems can be considered very reasonable.

## Conclusions

At low pressure methanol can be synthesized over gold-based catalyst with a CO conversion relatively low, however

by combining this later with a DME catalyst we are able to produce either products or mainly the dimethylether by enhancing significantly the CO conversion. This study has shown that this can be achieved by using 5%Au/ZnO/LZ-Y52 which manifests good catalytic activity towards direct dimethylether synthesis at moderately high temperature. Gold-based catalysts are clearly also capable of producing mixtures of methanol, DME and hydrocarbons, which could be attractive in a scenario where the synthesis of both fuel and petrochemical feedstocks is desired. The exact mode of hydrocarbon formation needs to be investigated in more detail, but initial work suggests that methanol (and/or DME) conversion may be the dominant pathway. Lower selectivities to methane might be achievable through a programme of catalyst design and process optimization.

## About the authors



**Professor Graham Hutchings** is a research professor in the School of Chemistry at Cardiff University. His research interests concern heterogeneous catalysis with a particular emphasis on catalysis by gold.



**Professor Mike Scurrill** is Professor of Physical Chemistry and Director of the Molecular Sciences Institute in the School of Chemistry at the University of the Witwatersrand. He conducts research in the field of heterogeneous catalysis, with current emphasis on catalysis by gold and

catalysis in energy conversion.



**Prof. Diane Hildebrandt** is Unilever Professor of Reaction Engineering, and is a Director of COMPS (Centre of Material and Process Synthesis) at the School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg, South Africa. Her postgraduate research groups work in the fields of distillation, bio-medical, attainable regions, process synthesis, industrial wastewater, catalysis and biotechnology.



**David Glasser** is Professor of Chemical Engineering, and is the Director of COMPS (Centre of Material and Process Synthesis) at the School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg. Research activities include distillation, bio-medical, attainable regions, process synthesis, industrial wastewater, catalysis and biotechnology.

**Arthur Mpela** has just completed his PhD degree and is now lecturing in the School of Chemical and Metallurgical Engineering at the University of the Witwatersand, Johannesburg.

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