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APPENDIX 1

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Year	Event	Researcher
1902	First report of the catalytic conver- sion of carbon monoxide and hydrogen; normal pressure process at 523K using nickel to produce methane.	Sabatier and Senderens [8,9]
1913	Patent granted for high pressure syn- thesis (100 atm) of hydrocarbons and oxygenated chemicals using a variety of catalysts.	Badische Anilin-und- Soda-Fabrik A. G. [10]
1922	Production of a mixture of oxygenated compounds at 100 atm. and 673K using alkalized iron-filings (Synthol process).	Fischer and Tropsch [138]
1923	Patents granted for controlled produc- tion of methanol exclusively on ZnO- Cr ₂ O ₃ at 200-300 atm. and 573-673K.	Badische Anilin-und- Soda-Fabrik A. G., Hanisch [11, 12, 139]
1925	Normal pressure synthesis of gasoline at 473-573K over Fe-ZnO and Co-Cr ₂ O ₃ catalysts.	Fischer and Tropsch [13]
1931	Ni-ThO ₂ -kieselguhr catalysts were developed that allowed the normal pressure synthesis at 448K instead of 523K.	Fischer and Meyer [140]
1932	Co-ThO ₂ -kieselguhr catalysts were developed that yielded much lower methane formation.	Fischer and Koch [141]
1935	Fischer-Tropsch yield increased by 10- 20% by doing the synthesis in steps with intermediate removal of products. The overall yield of methane was less with this process.	Fischer and Pichler [17]
1 9 36	Startup of first normal pressure full scale synthesis plant using Co catalyst (Oberhausen-Holten, Ger.)	

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Year	Event	Researcher
1936	Development of Co catalysts for a medium pressure (5-20 atm) moderate temperature (453-473K) process with more saturated products. The catalyst , did not require regeneration.	Fischer and Pichler [142]
1937	Medium pressure synthesis with Fe catalysts, 5-30 atm and 473-593K.	Fischer and Pichler [143, 144]
1938	Use of ruthenium catalysts at high pressure (50-1000 atm) and 373-473K to produce compounds with very high molecular weight.	Pichler [18]
1938	Oxo synthesis involving the conversion of olefins in the presence of CO and H ₂ to aldehydes.	Roelen [145]
1938	Start-up of first commercial Co medium pressure plant at Oberhausen-Holten, Germany.	Ruhrchemie
19 <u>4</u> 1	High pressure (150-600 atm) synthesis of branched hydrocarbons (isosynthesis) using ThO ₂ and other oxide catalysts at 673-773K.	Pichler and Ziesecke [146]
1943	Schwarzheide pilot plant studies of precipitated and fused Fe catalysts on the medium pressure synthesis.	KWI, Ruhrchemie, Rheinpreussen, Lurgi, Brabag, I. G.
1949	Carbon monoxide and water used as synthesis gas	Kolbel and Engelhardt [147, 148]
1950	Commercial scale medium pressure synthesis plant erected for conversion of CO and H ₂ from natural gas with Fe at Brownsville, Texas.	Hydrocarbon Research, Inc. and American Oil Companies.
1955	Start-up of Sasol-large scale synthesis plant in Sosolburg, South Africa for medium pressure synthesis using Fe.	South Africa Coal, Oil and Gas Corp., L. T. D.
1962	Synthesis of polymethylene from CO and H ₂ with activated ruthenium catalysts at high pressure below 423K.	Pichler and Firnhaber [1,49]

Year	Event	Researcher
1973	Copper catalysts developed that are more active than ZnO/Cr ₂ 0 ₃ for methane production.	[150, 151]
1974	Use of a homogeneous rhodium catalyst at 523K and extremely high pressures (1400-3500 atm) to selectively produce ethylene glycol.	Pruett and Walker [20]